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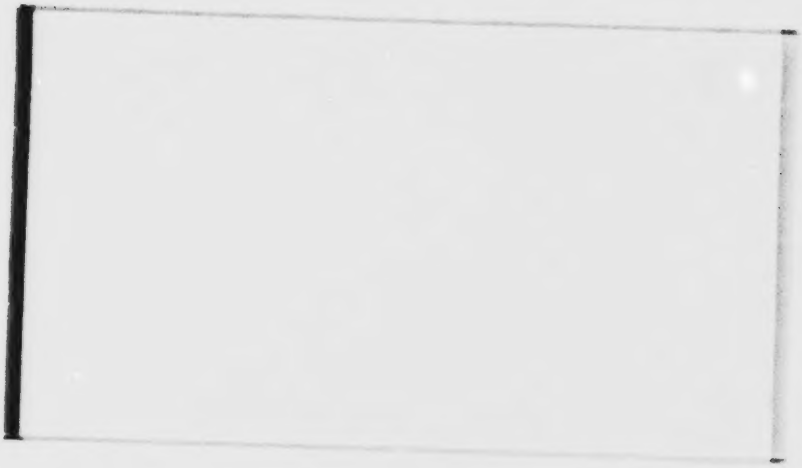

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PILOT SCALE STUDIES OF LIMESTONE INJECTION PROCESS - PHASE I: SIMULATING LAKEVIEW TGS QUENCHING RATE

Report No 86-62-K

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ABSTRACT

The limestone injection process for SO_2 control has been studied at Ontario Hydro's 620 MJ/h combustion research facility under conditions simulating the Lakeview TGS quenching rate. Various combinations of design and operating conditions affecting SO_2 and particulate removal have been evaluated using a non-porous local limestone, while burning a 1.7% sulphur eastern U.S. bituminous coal. The program is aimed at improving the overall efficiency of sulphur capture and sorbent utilization, and minimizing the impact of in-furnace injection on particulate removal by the ESP. The first phase of the program is complete. Process variables, such as sorbent injection location (which determines temperature and residence time), addition rate and particle size for a Beachville limestone have been optimized. At furnace quenching rates of 536°C/s and under optimized operating conditions, SO_2 removal efficiency was about

740631-335-600

job	file	date	report no.
740631-116-600 740631-711-600	837.241211	May 30, 1986	86-62-K

40 to 43% and sorbent utilization up to 17% was achieved. Under similar conditions, about 50% of the SO_2 could be removed from an SO_2-doped propane flue gas. The process produces finer and about twice as much ash as the coal. The carbon level of the waste on a sorbent-free basis is about 20%, resulting in 1.1% loss of the input heating value with the waste. Resistivity of the waste ranges between 10^5 to 10^6 ohm cm, up to one order of magnitude higher than that of the base-line coal ash. The ESP performed with a 10% reduced efficiency, probably because of the fineness of the waste and increased dust loading.

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EXECUTIVE SUMMARY

PILOT SCALE STUDIES OF LIMESTONE INJECTION PROCESS - PHASE I: SIMULATING LAKEVIEW TGS QUENCHING RATE

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Limestone injection into the furnace to reduce SO_2 emissions from coal fired utility boilers has been studied at Ontario Hydro's 620 MJ/h combustion facility, under conditions simulating the Lakeview TGS quenching rate. A highly volatile, 1.7% sulphur eastern U.S. bituminous coal and a non-porous limestone from Beachville, Ontario have been used in the study. The objectives of the program were to assess the effect of process variables on SO_2 capture, limestone utilization, ESP performance and waste characteristics and optimize these variables for maximum SO_2 capture, sorbent utilization and for improved ESP performance.

Rates of calcination and sulphation were estimated while burning propane gas: the calcination is complete within less than 300 ms, while the rate determining sulphation step is a much slower reaction. It was found that at about 1000°C, porosity and surface area of the calcine peaked and reactivity was the best.

Sulphur capture appears to be a very sensitive function of the temperature of the limestone injection site, limestone particle size and sorbent addition rate. The effect of residence time will be assessed in the next phase of the study. Response surface diagrams have been developed to correlate sulphur capture and sorbent utilization with operating variables. Under optimized operating conditions: at wall temperatures at the injection site of about 1000°C, limestone mass median diameter of 8.6 μm and Ca/S mole ratio of 2.5 to 3.0, 40 to 43% of the SO_2 could be removed from the flue gases. Sorbent utilization was 13 - 17%.

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The process produces about 2.2 times as much waste as the base-line coal. The limestone injection waste is finer than the coal ash and contains higher levels of carbon on a sorbent free basis. As a result about 1.1% of the input heat is lost in the waste as compared to 0.7% in the base line ash.

Dust loading to the ESP increased by a factor of 1.7. Due to the high levels CaO and $CaSO_4$ in the waste, resistivity increased by one half to one order of magnitude, to a maximum of 8.2×10^6 ohm.cm. The precipitator with an SCA of $15 m^2/m^3/S$ collected the waste with an efficiency of 81 to 85%. This efficiency is lower by about 10% than for the base line ash. The impaired ESP performance can probably be attributed to high dust loading and the fineness of the dust rather than to high ash resistivities. Based on the results of the study recommendations are made for future work.

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To Dr. W.R. Effer
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PILOT SCALE STUDIES OF LIMESTONE INJECTION PROCESS - PHASE I: SIMULATING LAKEVIEW TGS QUENCHING RATE

1.0 INTRODUCTION

The concept of injecting calcium-based alkaline sorbents directly into the furnace of coal-fired utility boilers to reduce SO_2 emissions is the subject of major development programs in the US and Europe. Ontario Hydro is contributing to these efforts by sponsoring a test program to develop a better understanding of fundamental process chemistry and optimize the process on the pilot scale for maximum SO_2 capture and sorbent utilization, and for improved precipitator performance.

This research program has been carried out in parallel with the planning and execution of the full scale tests of furnace injection at Lakeview TGS, and supplements the Lakeview tests.

The pilot scale study described in this report is considered the initial phase of a more comprehensive program that will include testing over a wider range of parameters, guided by the results from the initial work.

The furnace injection process involves the injection of pulverized calcium-based sorbent, such as limestone or calcium hydroxide directly into the furnace cavity of a coal-fired boiler. When exposed to furnace temperatures, the sorbent rapidly decomposes to form reactive calcium oxide (CaO) particles, which reacts with SO_2 to form calcium sulphate ($CaSO_4$). This $CaSO_4$ and the unreacted lime is collected with the fly ash in an electrostatic precipitator.

The following equations describe the principal reaction paths: The first step is the rapid decomposition of calcium carbonate in which the stone develops a porous structure that is essential in determining its reactivity. The second step is the rate determining sulphation step.

$$CaCO_3 \xrightarrow{\text{heat}} CaO + H_2O$$

$$CaO + SO_2 + 1/2\ O_2 \rightarrow CaSO_4$$

Ontario Hydro is developing this technology because of its potential as a relatively cheap SO_2 control option for existing power plants. Since it uses existing furnace cavities and particulate control devices for SO_2 reactions and removal, capital costs are expected to be much lower than those associated with wet scrubbers. Preliminary capital cost estimates range between $50 - $80/kW for retrofits in terms of 1984 dollars, depending on particulate collection/1/. Operating costs depend on sorbent utilization and coal sulphur content. Current sorbent utilization efficiencies are reported to be low resulting in high sorbent, solid-waste handling and disposal costs. Improving SO_2 removal efficiencies and sorbent utilization could greatly reduce the process operating costs./1,2,3/

Despite the low efficiencies reported to date, the ease with which this technique can be applied to existing power plants and the relatively low cost of running the process, have encouraged researchers to study ways of optimizing the process. Limestone injection is at a relatively early stage of development and substantial work is still required on every aspect of the process.

The following R&D areas were identified to resolve the major technical problems associated with the process:

- SO_2 Removal Efficiency and Sorbent Utilization. SO_2 capture is a complex physico-chemical process that is influenced by a variety of factors. The most important ones affecting sorbent utilization and SO_2 removal efficiency include: sorbent properties, particle size and stoichiometry, coal composition, temperature, residence time and sorbent mixing and dispersion in the furnace.

To-date, limestone utilization in pilot and full scale injection studies has been relatively poor. This is one area where more research and development is required. Higher sorbent utilization and SO_2 removal efficiency would result in reduced limestone and waste disposal costs, and wider applicability of the process.

Another issue is the potential impact the process will have on boiler and plant performance and operation which might include excessive particulate emissions, fouling, slagging and corrosion and increased waste management difficulties.

- Particulate Emissions. Calcium sorbent injection can double or triple solids loading to the boiler, depending on coal sulfur content, sorbent type, and Ca/S ratio. Greater solids loading increases ESP particulate inlet loading, while the calcium compounds in the ash increase ash resistivity. Together these factors can degrade ESP performance and result in high particulate emissions. This problem must be studied for a given sorbent and coal and means to improve precipitator performance by thermal and/or chemical conditioning must be developed.

- Boiler Slagging and Fouling. The addition of limestone or solid sorbents to the boiler can change the chemical and physical properties of the ash, thereby raising concerns about increased slagging and fouling on furnace heat transfer surfaces. Research to date indicates that these deposits can likely be managed with conventional soot blowing equipment, however, it is possible that additional soot blowers and/or more frequent use may be required. Field and pilot scale testing are required to provide further information on these characteristics.

- Ash Handling and Disposal. In-furnace calcium sorbent injection produces solid wastes greatly different from conventional ash. Unreacted sorbent, fly ash, and reaction by-products have different disposal characteristics and requirements which must be better understood. Specifically, the possible need for special handling, transport, pretreatment and disposal of the by-products must be identified before the technology can be widely employed. In parallel to the limestone injection tests, limestone modified ash samples from the pilot- and full-scale tests will be characterized and methods for safe disposal of the waste will be developed.

The overall objective of the pilot scale study is to further develop the limestone injection process under conditions simulating full scale operation, in order to understand the mechanisms that control sorbent utilization and to define

methods for increasing sorbent reactivity, maximizing SO_2 removal and improving ESP performance.

The specific objectives are as follows:

- To determine the operating conditions for the limestone injection process in order to achieve optimum SO_2 capture and sorbent utilization.

- To evaluate the electrostatic precipitator performance under optimum process conditions and develop methods to improve its performance.

- To assess the slagging and fouling potential on furnace heat transfer surfaces from increased ash loading and develop methods to improve heat transfer.

The initial test program was designed and carried out in such a manner that results relevant to the upcoming demonstration of limestone injection at Lakeview TGS were obtained first. This report summarizes the result of this initial phase, Phase I, of the program. In the second phase of the study applicability of this technology to Lambton TGS will be studied. Evaluating various sorbents, sorbent-additive mixtures, modes of sorbent injection, various coals and coal blends and ash conditioning agents will also be addressed in subsequent phases.

2.0 EXPERIMENTAL PART

2.1 Combustion Research Facility

The Combustion Research Facility (CRF) is designed for a maximum coal feed rate of about 20 kg/h US bituminous coal at a firing rate of 640 MJ/h, see Figure 2-1/4/. The furnace is a refractory-lined cylindrical chamber, fully equipped for monitoring gas and wall temperatures. There are multiple ports for flame observation and for insertion of solid sampling probes. There are also probes to determine slagging and fouling rates. Pulverized coal is delivered down-draft to the burner with the combustion air, which can be electrically preheated to temperatures up to 350°C. Gas burners on each side of the coal burner are used to heat the furnace to operating temperatures before beginning to feed the coal.

The coal burner, designed and constructed by Research Division staff, is equipped with a vortex generator and four air vanes to assure good mixing and adequate residence time of the fuel-air mixture in the combustion zone. The combustion gases in the

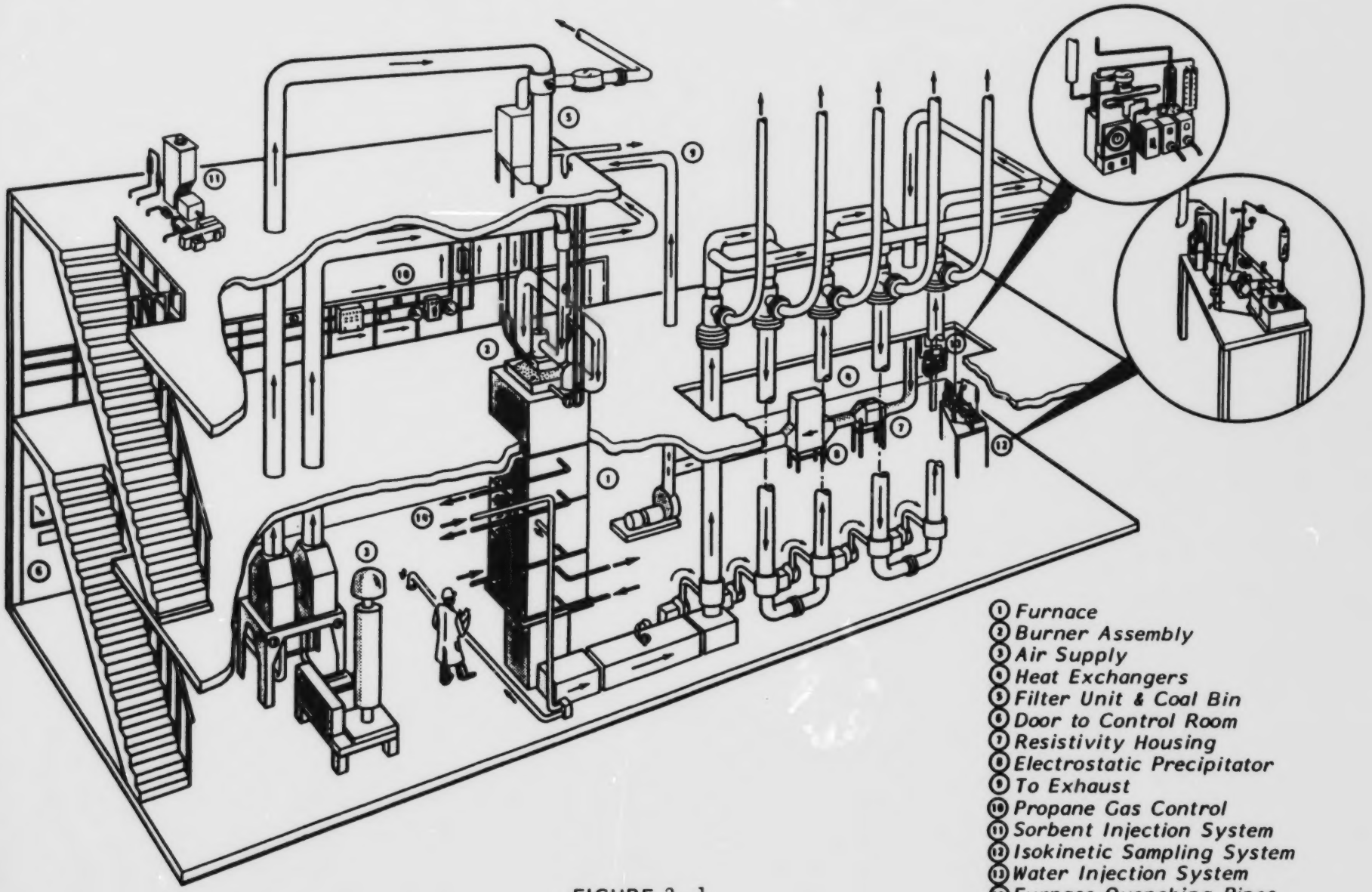


FIGURE 2–1

COMBUSTION RESEARCH FACILITY

furnace are cooled by water and/or air circulating in a cylindrical inconel jacket around the furnace. This cooling system is equipped with temperature sensors and flow meters to control furnace quenching rates.

The combustion gases leaving the furnace are further cooled by a series of air-cooled heat exchangers to between 90-400°C prior to entering the resistivity probe housing and electrostatic precipitator (ESP).

The ESP consists of a cubical stainless steel chamber, and is equipped with two sets of interchangeable cells. One set has an eleven plate electrode with 2.5 cm spacing, the other a five plate electrode with 5 cm spacing. The ESP can operate up to a temperature of approximately 400°C. The design specific collection areas (SCA, $m^2/m^3/s$) for the two sets of cells are 33 and 15 respectively for base line firing conditions using a highly volatile US bituminous coal.

Particulate mass loading in the flue gas before and after ESP is measured with an isokinetic sampling system (Figure 2-2). The in-situ resistivity of the fly ash is determined with a point-plane resistivity probe, situated in the resistivity probe housing.

The CRF instrumentation permits system temperatures, and flue gas compositions to be monitored continuously. Temperatures are measured with thermocouples and flame temperatures with an optical pyrometer. Flow rates and pressures are measured by flow meters and manometers. Flue gas compositions are continuously monitored, after removing the moisture from the stream by a sample conditioner. Flue gas instrumentation includes O_2, CO_2, CO, SO_2 and NO_x analyzers. These data are recorded continuously for the duration of a run. All the measuring and monitoring systems are linked to a computerized data acquisition system. Specialty calibration gases in compressed gas cylinders are used for calibration of the flue gas instruments to the same approximate gas concentration as the flue gas.

To meet the objectives of the limestone injection test program, the CRF had to be modified and equipped with suitable instrumentation. A detailed description of these modifications is given in Reference 5. The following modifications to the facility have been carried out:

- Modification to the combustion gas cooling. By installing a cylindrical inconel jacket (water and/or air cooled) around the furnace, complete with instrumentation for measuring

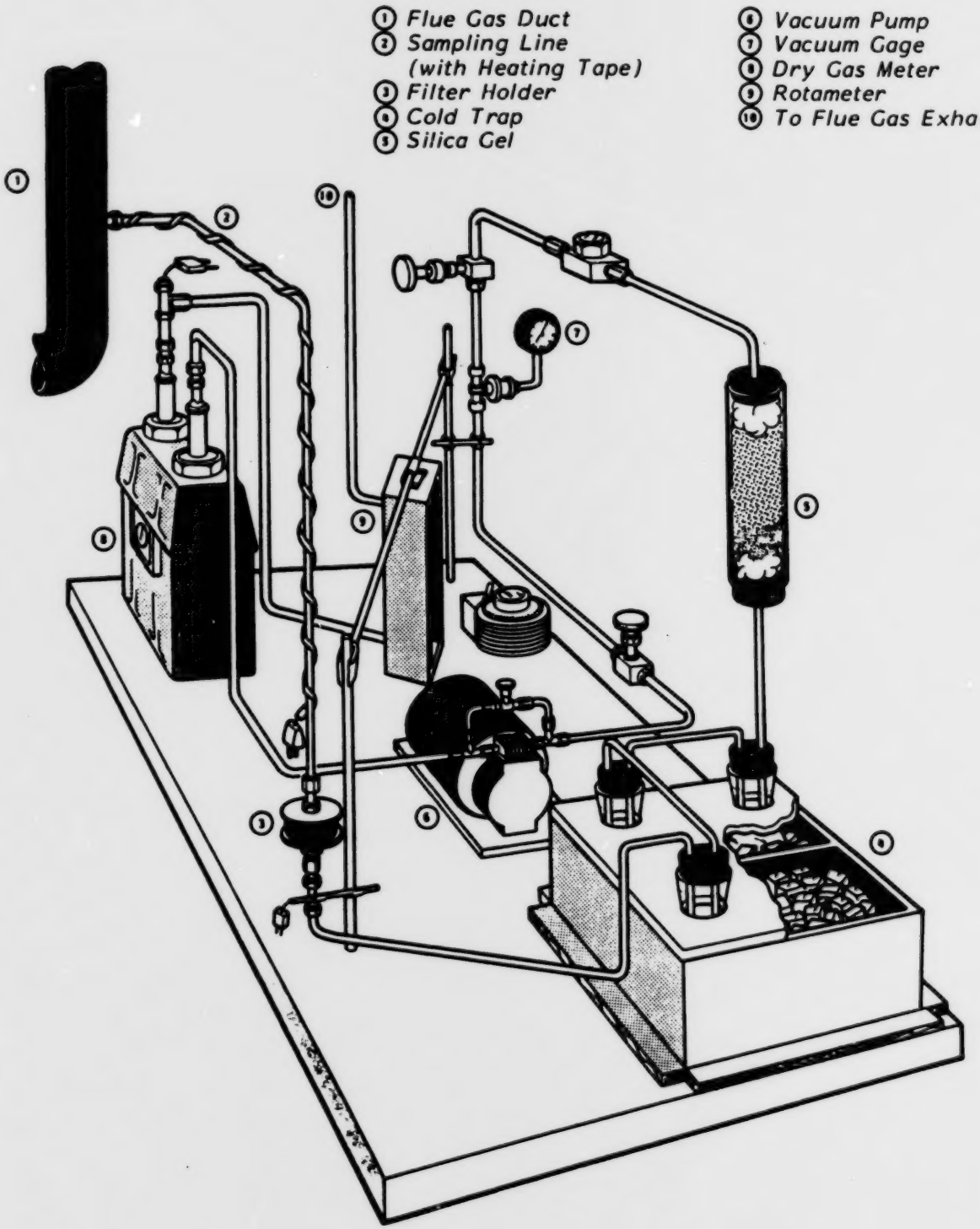


FIGURE 2-2
ISOKINETIC SAMPLING SYSTEM

water and air flows to the jacket and temperatures, cooling rates similar to those obtained in the boilers at Lakeview or Lambton TGS can be achieved (Figure 2-3). Furnace quenching rates before and after installing the jackets are given in Table 2-1. The temperature-time and radial temperature profiles of the modified furnace are given in Figure 2-4.

- Sorbent injection system (Figure 2-5). This system consists of sorbent injection ports installed at five locations along the length of the furnace and a storage and feeding system for sorbents and additives. Photograph 1 shows the injection nozzle in the furnace spraying limestone.

- Water injection system. This is located ahead of the resistivity probe housing in order to cool and humidify the flue gas before allowing it to enter the electrostatic precipitator (Figure 2-6). This will allow study of the performance of the electrostatic precipitator with moisture conditioning under increased particulate loading from injected limestone.

2.2 Sampling and Analysis

(a) Solid Sampling from the Furnace

Solid sampling from the furnace was done for gas firing only. A series of experiments were conducted with propane gas firing to develop a better understanding of the calcination and sulphation processes. In one set of experiments, limestone was injected into the gas stream at various injection locations and the rate of decomposition was determined as a function of residence time in the hot zone. A solid sample was withdrawn from the furnace in a 1.27 cm diameter inconel sampling probe by means of a vacuum pump and collected on a glass-fibre filter (photograph 2). The collecting filter was heated to 120°C to avoid condensation and hence minimize in-probe reaction. In another set of experiments the flue gas was doped with SO_2 at levels corresponding to about 1.7% S in coal at a firing rate of about 350 MJ/h. The rate of sulphation was determined by analyzing solid samples, withdrawn at various locations in the furnace for Ca/S ratios. The solid samples collected were analyzed by Ontario Hydro's Chemical Research Department. Calcines were analyzed for their $CaO/CaCO_3$ ratios. CaO was determined by following the procedure outlined in ASTM C471-76 and sulphur by the Leco Induction furnace. Porosity, pore size distribution, particle mass median diameter (MMD) and BET surface areas of the samples was performed by the Ontario Research Foundation as described in section 2.2(f).

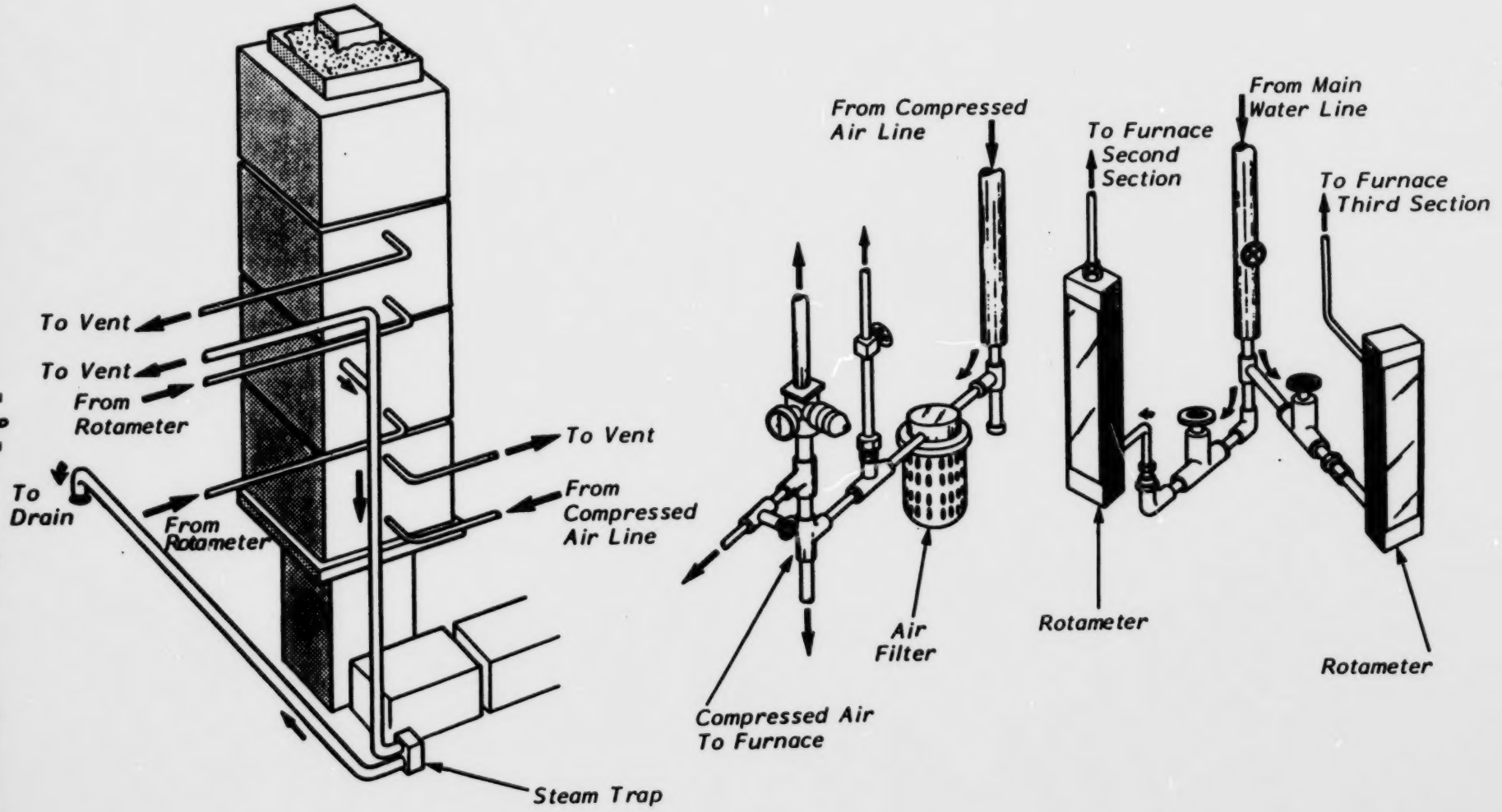


FIGURE 2-3

FURNACE QUENCHING SYSTEM

TABLE 2-1

FURNACE QUENCHING RATES

Temperature Range 1150-850°C / CRF and Full Scale Boilers	Quenching Rate °C/s	Residence Time s
CRF (before quenching)	136	2.2
CRF (with maximum quenching)	536	0.56
*Lambton TGS	320	0.94
*Nanticoke TGS	566	0.53
*Lakeview TGS	555	0.54

* Data Obtained from Reference 6.

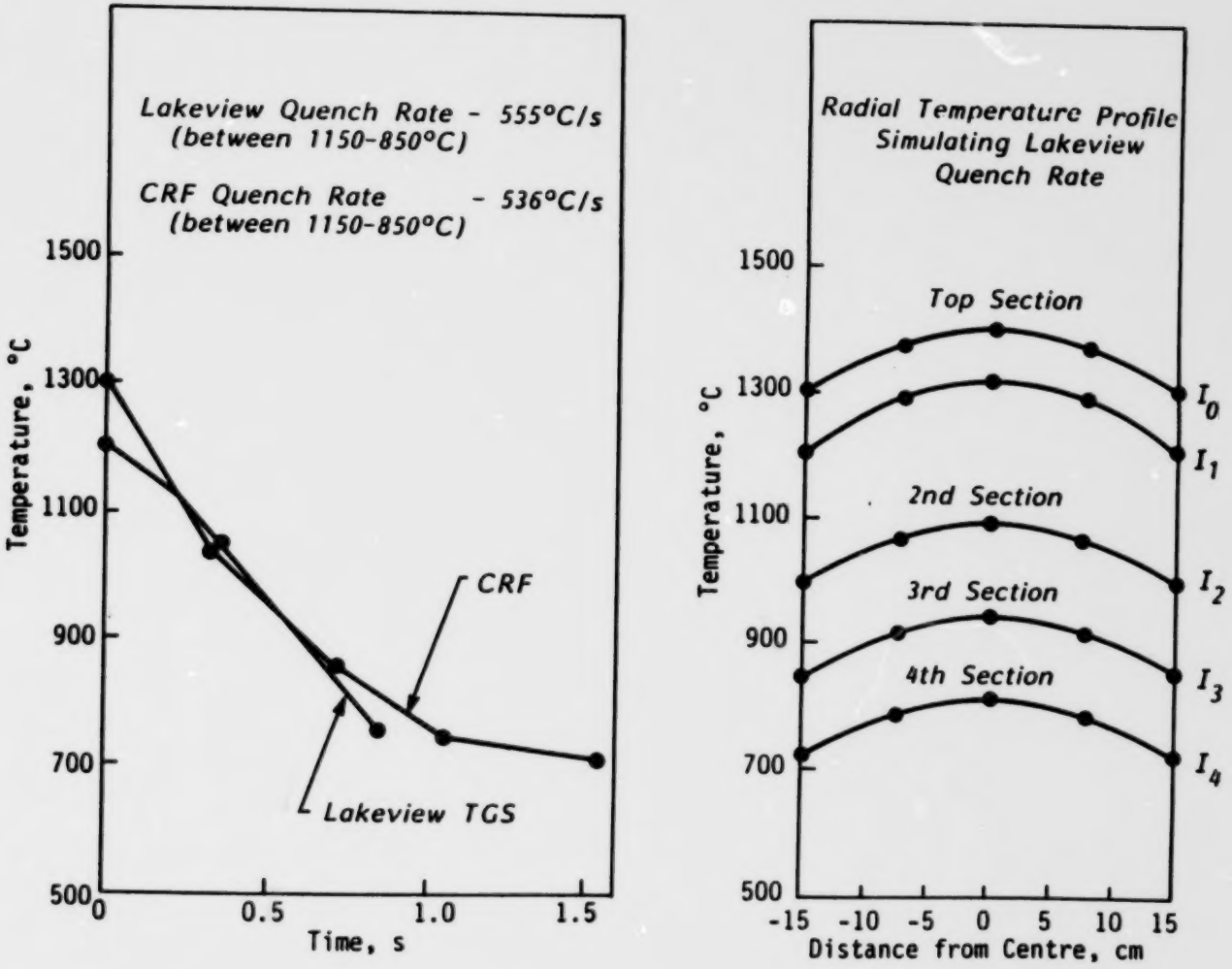


FIGURE 2–4

TEMPERATURE-TIME AND RADIAL PROFILES OF FLUE GASES

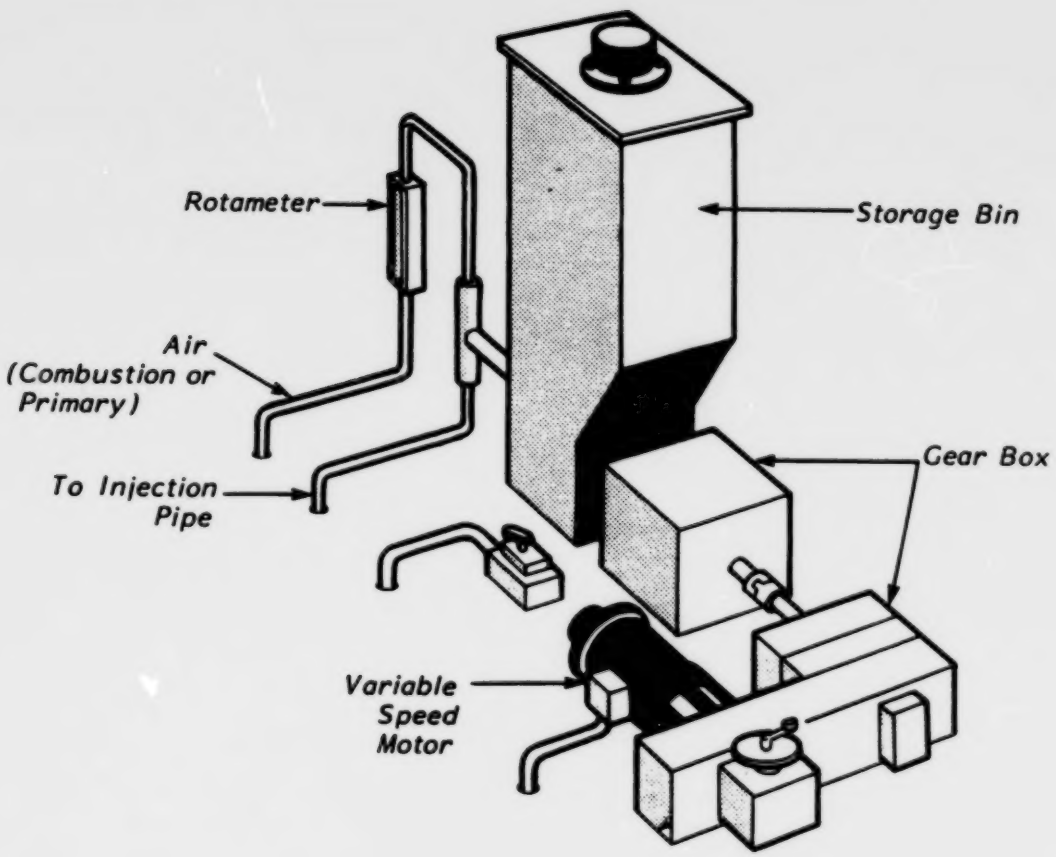


FIGURE 2-5
SORBENT INJECTION SYSTEM

PHOTOGRAPH 1
SORBENT INJECTION NOZZLE

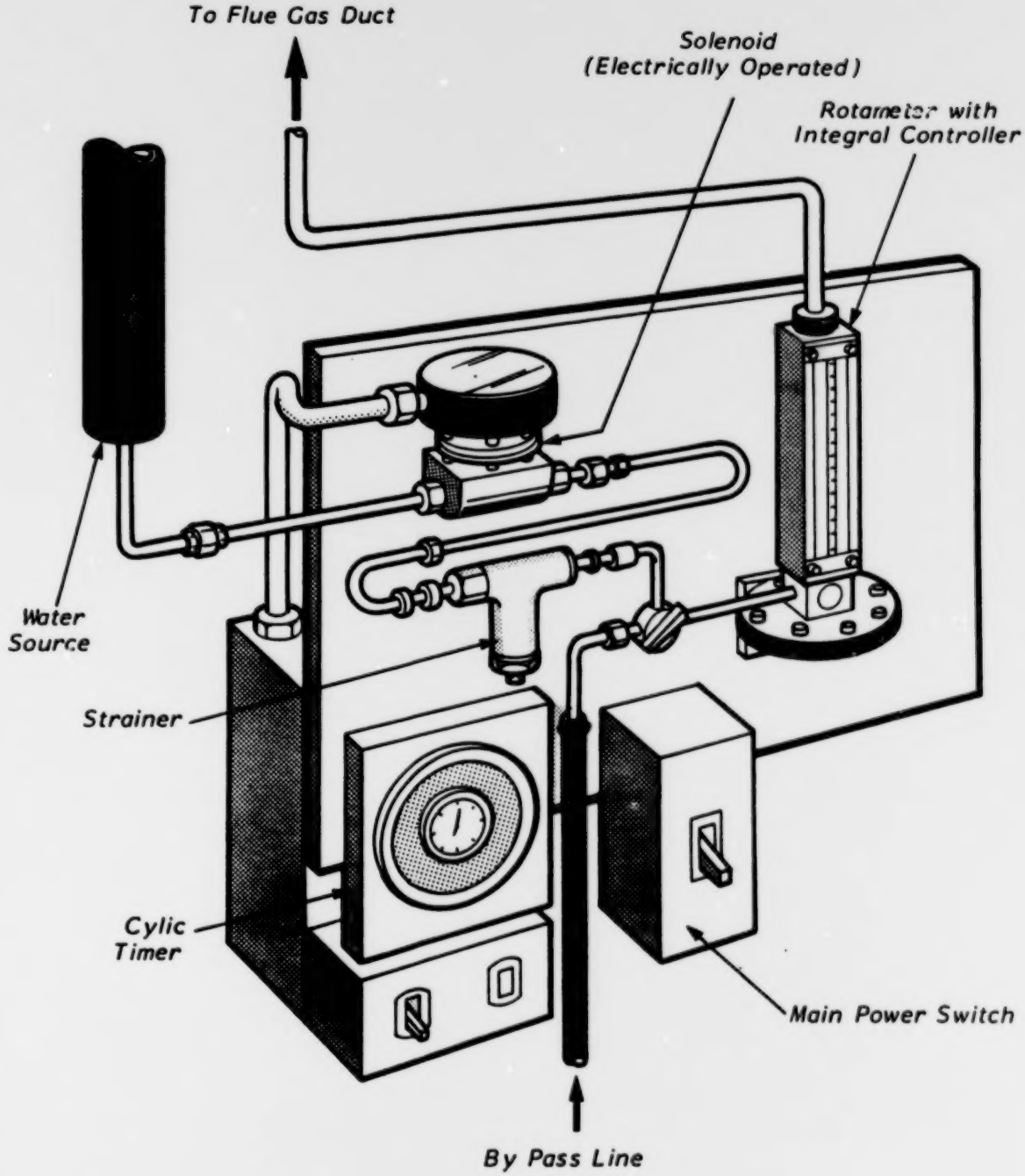
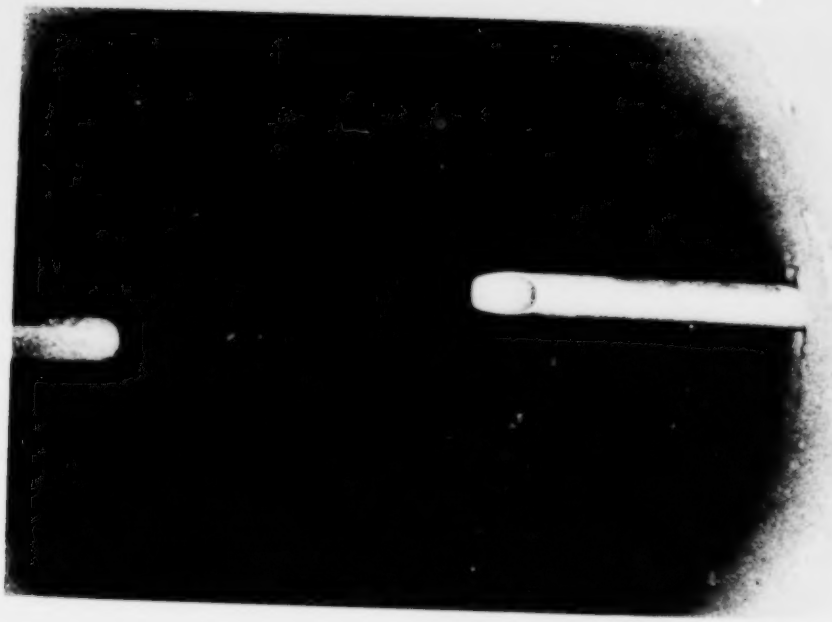


FIGURE 2-6
WATER INJECTION SYSTEM



PHOTOGRAPH 2
SOLID SAMPLING PROBE

(b) Isokinetic Sampling System

Isokinetic sampling of fly ash was done before and after the precipitator in order to determine dust loading and precipitator performance. Samples collected were also used in all ash analyses. A pitot tube located near the 1.27 cm gooseneck nozzle measured the gas velocity in the duct. Once the velocity was established, the gas flow rate through the nozzle was monitored at ambient temperature and corrected for in-stack temperature conditions. The exact volume of gas sampled was recorded by a dry gas meter. Fly ash samples were collected on a glass fibre filter and during sampling the sampling line was heated to stack temperature to avoid water condensation.

(c) Continuous Gas Analysis

Flue gas was continuously withdrawn through an in-stack stainless steel probe at a point where the temperature was approximately 650°C. The gas then passed through a refrigeration unit which removed water by condensation at a temperature of approximately -10°C. The length of the sampling line was made as short as possible and was heated to 120°C to avoid any condensation. The sampling line was cleaned after every test. Solid samples collected from the sampling line and samples taken from the furnace showed no significant differences in Ca/S ratio. Condensate collected during gas firing with injection of limestone contained negligible calcium and the equivalent of maximum 2.3% of the gas phase SO_2. The suitability of this sampling system has also been demonstrated by injecting standard SO_2 just ahead of the sample probe and observing its recovery. The SO_2 recovery was 98-99%.

(d) Coal Analysis

A high volatile eastern US bituminous coal from Lakeview TGS was used in the study. Coal samples were analyzed to determine ultimate and proximate analysis, heating value and particle size distribution (Table 2-2 and Figure 2-7). Analyses and particle size distribution of coal samples from the CRF and Lakeview TGS are similar.

For the ultimate analysis carbon and hydrogen gas was determined by the method described in Reference 8. Sulphur was done by the Leco Induction method and nitrogen by the Kjeldahl method as outlined in ASTM D3179. Oxygen was calculated by difference as the last remaining constituent.

Proximate analysis was performed according to ASTM method D3173-D3175 and the calorific value by ASTM method D3286, using

TABLE 2-2

CHARACTERISTICS OF US BITUMINOUS COAL

Proximate and Ultimate Analysis

Proximate, g/kg				Ultimate, g/kg (moisture free basis)					
Moisture	Ash	Volatile Matter	Fixed Carbon	C	H	N	S	O	Heating Value MJ/kg
14	80	357	548	756	57	16	17	74	32

Particle Size Distribution

Sieve Opening µm	Cumulative % Undersize	
150	100	*89
106	93	
75	73	*72
63	59	
53	56	
45	51	
<44	-	

* Lakeview TGS results

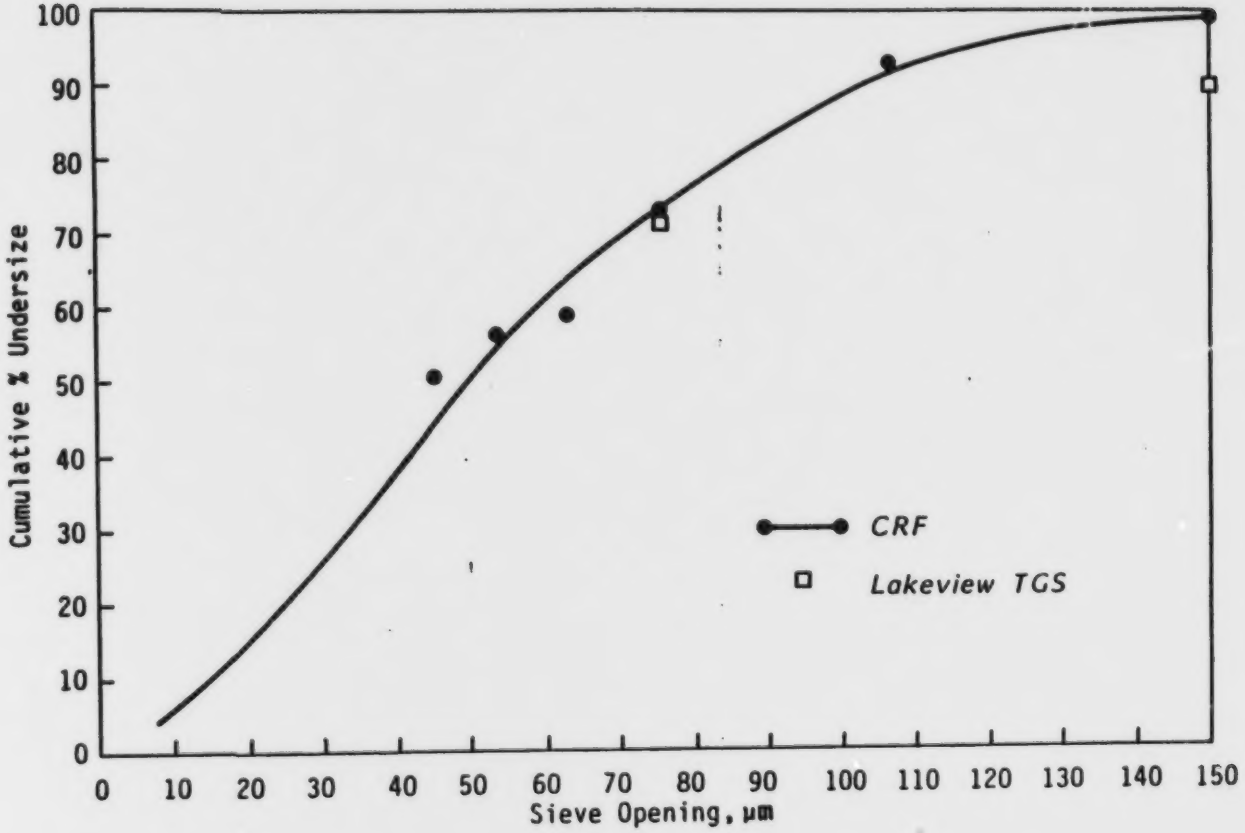


FIGURE 2-7

PARTICLE SIZE DISTRIBUTION OF EASTERN U.S. BITUMINOUS COAL

an adiabatic bomb calorimeter. Particle size distribution was determined by sieve analysis according to ASTM method D-197.

(e) Ash Analysis

Ash samples collected isokinetically before and after the electrostatic precipitator were analyzed for major mineral oxide concentrations (Al, Si, Na, Mg, Ca, K, Fe, and S), as outlined in Reference 7.

The fusion temperatures of the ash samples were determined in accordance with ASTM method D1857.

Particle size distributions were determined by the method outlined in ASTM procedure D422.

The concentration of mineral oxides, fusion temperatures and particle size distribution of an ash sample obtained at the CRF under base line firing conditions and from Lakeview TGS are given in Table 2-3, and Figure 2-8 respectively. As indicated by the data, chemical composition, ash fusion temperatures and particle size distribution of ash samples from Lakeview TGS and CRF are very similar.

(f) Sorbent Characteristics

A calcitic limestone from the Beachville area was selected for this phase of the study. The concentration of major mineral oxides was determined by the method used for the ash and particle size distribution was done by the method outlined in ASTM procedure D422. Mass median diameter was done by image analysis and by sedigraph. Solid density by liquid pycnometry and porosity was obtained by mercury intrusion porosimetry measurements. Surface area was obtained by gas adsorption (B.E.T.). These analyses were carried out at the Ontario Research Foundation except the particle size distribution and mineral oxides concentration which was done by the Civil and Chemical Research Departments of Ontario Hydro. The physical and chemical characteristics of the limestone are given in Table 2-4 and particle size distribution for various grinds used in this study is plotted in Figure 2-9.

2.3 Base Line Firing Conditions

(a) Gas Firing

The down-fired combustor is heated with propane gas overnight at a rate of about 240 MJ/h achieving temperatures in the range of 900-1000° C on the morning of the planned test. The gas is then

TABLE 2-3
CHARACTERISTICS OF EASTERN U.S.
BITUMINOUS COAL ASH

Chemical Composition, g/kg

	Base line Ash (CRF)	Lakeview TGS Ash Sample*
Na_2O	6	5
K_2O	17	14
MgO	9	7
CaO	50	31
Fe_2O_3	77	128
Al_2O_3	215	225
SiO_2	451	453
SO_3	23	10
LOI	161	179

Ash Fusion Temperatures, °C
Reducing Atmosphere

	Base line Ash	Lakeview TGS Ash*
Initial Deformation Temperature, IT	1240	1280
Softening Temperature, ST	1270	1300
Hemispherical Temperature, HT	1290	1320
Fluid Temperature, FT	-	1450

Particle Size Distribution of the Ash

Sieve Opening µm	Cumulative % Undersize	
	CRF	*Lakeview
7	10	26
17	54	60
37	68	78
44	92	85
75	96	92
105	98	96
250	100	100

* Sample from Lakeview TGS obtained June 27, 1984, from Cegrit sampler.

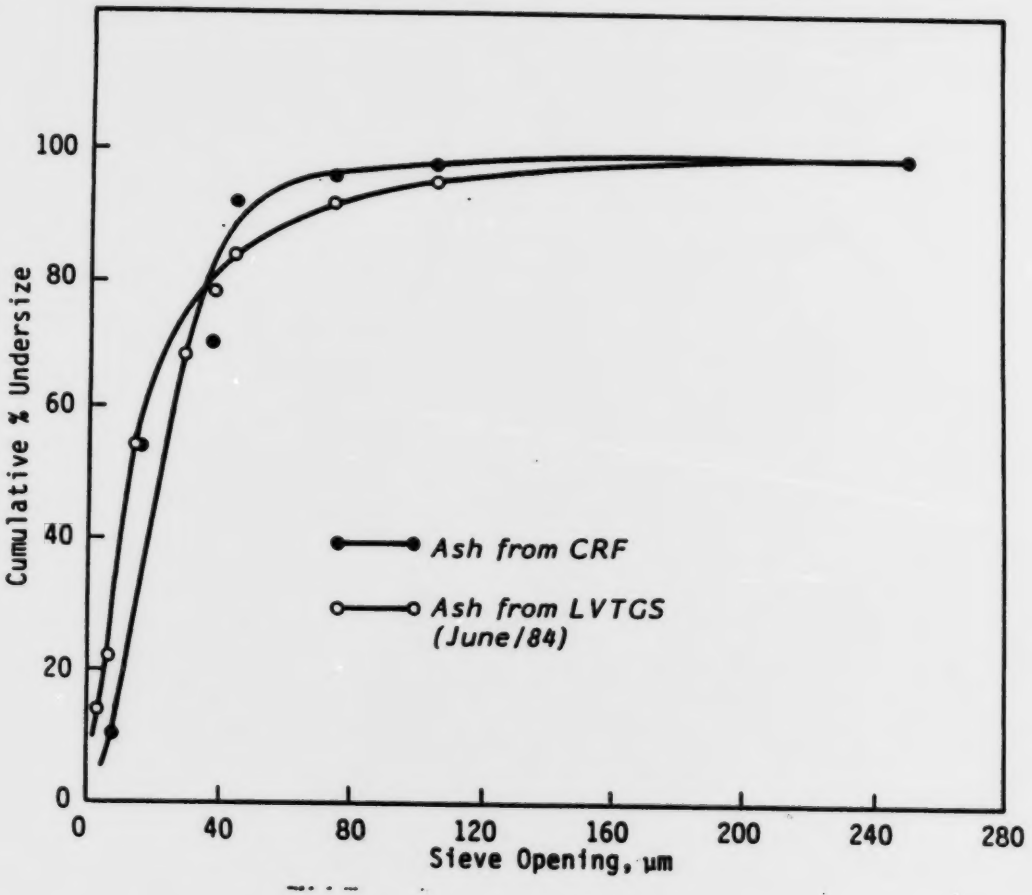


FIGURE 2-8

PARTICLE SIZE DISTRIBUTION OF FLY ASH
FROM U.S. BITUMINOUS COAL

Table 2-4

CHARACTERISTICS OF BEACHVILLE LIMESTONE

Chemical and Physical Properties

Li_2O, g/kg	<0.03
Na_2O	0.03
K_2O	0.6
MgO	8.0
CaO	524.0
Fe_2O_3	0.1
Al_2O_3	22.0
SiO_2	<12.0
SO_3	
LOI	434.0
BET area, m^2/g	1.3
MMD, μm_3	8.6
ρ, g/cm^3	2.6
Porosity, %	17.0

Particle Size Distribution

Sieve Opening µm	Cumulative % Undersize (MMD, µm)		
	10.5	8.6	4.4
150	97	100	100
106	95	99	100
75	90	98	99
63	89	97	98
53	87	95	97
45	84	93	96
37	81	90	94

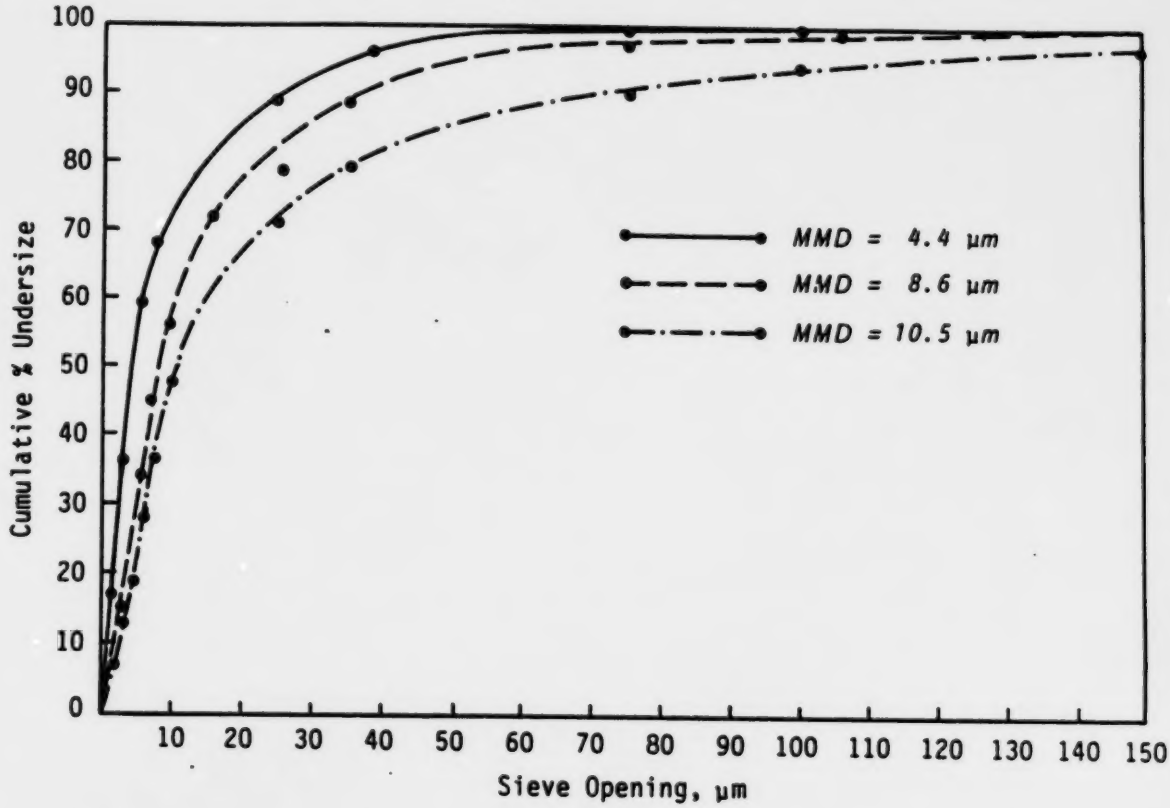


FIGURE 2-9

PARTICLE SIZE DISTRIBUTION
BEACHVILLE LIMESTONE

boosted to approximately 350 MJ/h and temperatures in the range 1300 - 1350° C are obtained. Furnace quenching is adjusted and the system allowed to stabilize before flue gas measurements are recorded. The calcination and sulphation experiments conducted with propane gas firing are described in Section 3.1.

Typical propane gas firing conditions are given below:

Gas firing rate	~ 350 MJ/h
Primary air flow	= 0.14 m^3/min at 25° C
Secondary air flow	= 0.8 m^3/min at 250° C

Furnace wall temperature profile:	top section	~ 1300° C
	2nd section	~ 1080° C
	3rd section	~ 850° C
	4th section	~ 720° C

Flue gas composition	O_2	~ 5%
	CO_2	~ 12%
	CO	~ 25 ppm
	SO_2	= 1450 - 1550 ppm (with doping)

(b) Coal Firing

Coal was fired at a rate of ~13 kg/h. All tests were performed with an eastern US bituminous coal. Upon attaining the desired quench rate the switch from propane to coal was made. The system was allowed to come to steady-state for the desired quench rate and the baseline SO_2 concentration in the flue gas was recorded as the average over a two-minute span as indicated by the SO_2 monitor. Typical base line firing conditions are as follows:

Nominal coal firing rate	~ 420 MJ/h (~ 13 kg/h)
Primary air flow	~ 0.8 m^3/min at 100°C
Secondary air flow	~ 2.4 m^3/min at 250°C

Furnace wall temperature profile:	top section	~ 1350°C
	2nd section	~ 1040°C
	3rd section	~ 880°C
	4th section	~ 725°C

Flue gas composition:	O_2	~ 5%
	CO_2	~ 14%
	CO	~ 100 ppm
	SO_2	~ 1400 ppm
	NOx	~ 540 ppm

Loss on ignition: 15 - 16%
(Complete ash analysis is given in Table 2-3.)

After reaching steady-state firing conditions, the sorbent feeder was started and the reduced SO_2 level in the flue gas was taken as the first stable two-minute average after sorbent injection. To ensure the elimination of a possible bias due to sorbent build-up on the furnace walls and in the sampling line,the SO_2 levels in the gas were required to return to base line conditions in just over five minutes of the cessation of sorbent feeding. Any questionable results were discarded and the test repeated. To correct for slight variations in furnace conditions, all SO_2 concentrations were normalized to 5% excess oxygen.

3.0 RESULTS AND DISCUSSION

3.1 Gas Firing - Calcination and Sulphation Studies

(a) Theoretical Background

It is generally accepted that the heterogeneous reaction between solid limestone and gaseous SO_2 involves two main chemical steps: the fast decomposition of calcium carbonate to calcium oxide and the relatively slow rate determining sulphation step. The reaction scheme however is extremely complex due to the several mass transfer, heat transfer and chemical reactions involved in the process: (Fig 3-1).

1. Mass transfer, either through molecular or turbulent diffusion of the gas phase reactant SO_2 from the bulk of the gas stream to the external surface of the solid lime particle.

2. SO_2 gas-solid interaction which may consist of:

   (a) Gaseous reactant diffusion through the internal pores of the solid.
   (b) Physical adsorption of the gaseous reactant on the surface of the internal pores of the solid.
   (c) Chemical reaction between SO_2 and CaO at the surface of the internal pores of the solid. The increased bulk of the reaction product would lead to decreased pore sizes and increased length of pores for reactants to reach reactive surfaces. The small reverse reaction decomposition of ($CaSO_4$ or $CaSO_3$) would also lead to desorption of the product ($CaSO_4$ and $CaSO_3$) from the surface of the internal pores.
   (d) Diffusion of the products through the pores of the solids to the external surface and their decomposition.

3. Mass transfer of the decomposition products from the external surface of the solid to the bulk gas stream.

Steps 1 and 3 are diffusion controlled while step 2 is a function of the temperature, physical properties and reactivity of the adsorbent.

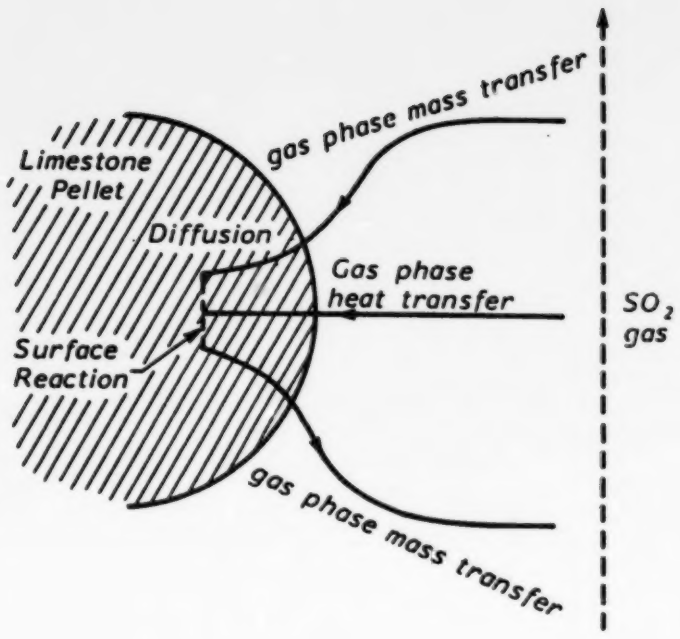


FIGURE 3-1.
REACTION BETWEEN LIMESTONE PELLET AND SO_2 GAS

The reaction is probably limited by either one or a combination of the following steps: gas phase mass transfer of SO_2; pore diffusion or mass transfer of gaseous SO_2 through the solid reactant (lime) or product (sulphated lime) and chemical reaction.

Kinetic measurements have indicated that the sulphation step is first order with respect to SO_2 and zero order with respect to oxygen/9/. It is also well documented that the sulphation rate decreases with the extent of reaction, suggesting that the reaction rate is indeed strongly affected by the diffusion of the gaseous reactants into the particle. Because $CaSO_4$ has a molar volume of about three times that of CaO, the accumulation of reaction products on the calcine surface causes the porosity to decrease and the diffusional resistance to increase/10,11,12/.

Various models have been proposed which describe the extent of conversion as a function of the physical and chemical characteristics of the solid and gaseous reactants. Most of these models point out that when the pore mouths are filled with the reaction products, a considerable percentage of the pores could become inaccessible to the gaseous reactants and reaction could stop.

In an attempt to improve our understanding of the calcine properties that affect reactivity and to assess rates of calcination and sulphation, a series of tests were conducted at the CRF using propane gas as fuel. This relatively "clean" system enabled us to collect solid samples from the furnace not contaminated with coal ash. Properties of calcine and sulphated lime samples (chemical composition, specific surface area, pore size distribution) and the rates of calcination and sulphation could thus be assessed.

(b) Objectives of Tests

The limestone was injected first into the flue gas and later into the SO_2 doped flue gas to study the rate of calcination and sulphation of the stone under conditions simulating full-scale operations (Lakeview TGS quench rate). The objectives were as follows:

- To study the kinetics of calcination and sulphation of a Beachville limestone as a function of injection temperature and residence time in the temperature zone: 1150-850°C.
- To evaluate the physical properties of the calcine such as surface area, porosity and pore size distribution as a

function of injection temperature. These properties are known to be critical in determining the effectiveness of the stone for sulphur capture.

- To examine the calcine and sulphated product microscopically and by mercury porosimeter and to establish whether sintering or pore plugging occur.

- To compare the rate of sulphation of the stone between propane combustion gases doped with SO_2 and coal combustion gases to evaluate any deactivation of the stone that might take place through interaction with coal mineral matter.

(c) Results

The results of the calcination and sulphation tests conducted with gas firing are summarized in Tables 3-1 and 3-2. For the calcination tests pulverized limestone, MMD = 8.6 μm was injected into the furnace at locations I_1 and I_2. Furnace wall temperatures at these locations are about 1200°C and 1000°C respectively. The temperatures at the centre of the furnace are higher being approximately 1300°C and 1100°C for I_1 and I_2 respectively. The calcined samples were collected at S_2, S_3 and S_4, thereby providing increasingly longer residence times for the calcination at temperature levels ranging from 1200 to 850°C. In the sulphation tests the same limestone was injected at location I_1 and I_2 into an SO_2 doped gas flame. The concentration being 1450 to 1550 ppm. In a few cases, samples were collected at sampling sites S_2, S_3 and S_4 in an attempt to evaluate the effect of residence time on sulphur capture in the sulphation zone. The calcine samples were analyzed for CaO and $CaCO_3$ content and their physical characteristics, such as porosity, BET-surface area, density and mass median diameter (MMD) were determined. The sulphated samples were analyzed for Ca and S content.

It has to be emphasized that since these samples were not collected isokinetically the results should be considered semi-quantitative.

The rate of calcination, molar conversion of $CaCO_3$ to CaO and of sulphation, conversion to $CaSO_4$ are plotted in Figure 3-2. The results obtained have shown that at temperatures above 1000°C, calcination is more than 95% complete in less than 300 ms. Sulphation appears to be a much slower reaction. However, to determine the exact rates of calcination and sulphation and to examine the effect of sorbent characteristics, gas environment and initial particle size distribution on the calcination and sulphation processes more fundamental work will be conducted in a small scale plug-flow reactor.

TABLE 3-1

GAS FIRING - CALCINATION AND SULPHATION TESTS

Beachville limestone: porosity = 17%, BET surface area = 1.3 m^2/g, MMD = 10.5 μm
Furnace quenching rate = 536°C/S

a. Calcination

Run No	Injection		Sampling		Calcine					Extent of Calcination, $\frac{\text{moles CaO}}{(\text{CaO+CaCO}_3)} \times 100$
	Location	Temp, T_I °C	Location	Temp, T_s °C	Residence Time, T_I-T_s	Porosity %	Mass Median Diameter, μm	Solid Density, g/cm^3	BET Surface Area, m^2/g	
CL-12	I_1	1200	S_2	1000	0.28	25	15.5	2.26	3.6	99
CL-05	I_2	1010	S_3	880	0.26	43	13.7	2.40	9.1	95
CL-08	I_2	1000	S_3	880	0.24	48	17.4	1.70	11.6	96
CL-07	I_2	1030	S_4	750	0.72	41	15.5	2.15	6.9	97

b. Sulphation

SO_2 in flue gas -1450-1550 ppm

Run No	Ca/S Mole Ratio	Injection		Sampling			Solid Sample	SO_2 Capture % (a)
		Location	Temp, T_I °C	Location	Temp, T_S °C	Residence Time, T_I-T_s	S/Ca Mole Ratio	
S-02	2.5	I_1	1200	S_2	1000	0.28	0.017	47.5*
S-03	2.5	I_1	1200	S_3	880	0.52	0.042	48.2*
S-04	2.5	I_1	1200	S_4	750	0.94	0.046	34.2
S-05	2.5	I_2	1000	S_4	750	0.74	0.111	54.8
S-06	2.5	I_2	1000	S_3	880	0.24	0.096	50.8

(a) based on flue gas analysis

* These were the first two runs carried out with limestone injection and not enough attention was paid to the proper sampling procedures (gas lines were not cleaned and the sampling line was not heated).

TABLE 3-2 SUMMARY OF RESULTS

Normalized to 3% oxygen.

RUN NO	FUEL TYPE	FUEL FIRING RATE MJ/H	QUENCH RATE DEG C/S	SORBENT PART. SIZE MICRON	SORBENT CA/S RATIO	INJECTION LOCATION	INJECTION TEMP DEG C	INJECTION RES. TIME S	FLUE GAS COMPOSITION CO2 %	FLUE GAS COMPOSITION O2 %	FLUE GAS COMPOSITION CO PPM	FLUE GAS COMPOSITION NOX PPM	FLUE GAS COMPOSITION SO2n DRY PPM	FLUE GAS COMPOSITION SO2n WET PPM	SO2 REM %	SORBENT UTIL %	ASH LOI %	ASH RES. OHM-CM	DUST L BEFORE ESP G/M3	DUST L AFTER ESP G/M3	ESP PERFORMANCE SCA M2/M3/S	ESP PERFORMANCE FIELD STRENGTH KV/CM	ESP PERFORMANCE EFF. %
S-01	GAS	350	536	0.6	3.0	11	1200	0.60	11	5.5	30		1523	800	47	16							NA
S-03	GAS	350	536	0.6	3.0	11	1200	0.60	11	5.3	30		1498	776	48	16							NA
S-04	GAS	350	536	0.6	3.0	11	1200	0.60	10	5.3	26		1498	987	34	11							NA
S-05	GAS	350	536	0.6	3.0	12	1000	0.33	13	4.5	25		1527	668	56	19							NA
S-06	GAS	350	536	0.6	3.0	12	1000	0.33	12	5.0			1575	775	51	17							NA
S-07	GAS	350	536	0.6	3.0	12	1000	0.33	12	5.0			1575	775	51	17							NA
S-22	GAS	350	536	0.6	2.5	13	850		11	5.0	26		1510	762	43	17							NA
S-23	GAS	350	536	0.6	2.5	12	1000	0.33	11	5.3	25		1270	635	50	20							NA
S-24	GAS	350	536	0.6	2.5	12	1000	0.33	10	5.5	30		1344	731	47	19							NA
S-24	GAS	350	536	0.6	2.5	11	1200	0.60	11	5.0			1275	525	37	11							NA
S-25	GAS	350	536	0.6	2.5	10	1350	0.72	11	4.8			1255	640	30	12							NA
LU-02	US-COAL	420	536						15	3.5	170		1425	NA	68	NA	16	2.40E+05	3.4	0.4	15	2.4	89.50
LU-03	US-COAL	420	536						15	4.0	150	540.0	1450	NA	68	NA	15	5.10E+05	3.3	0.3	15	2.4	92.60
LU-01	US-COAL	420	536	0.6	2.5	12	985	0.25	14	5.3	150		1270	723	43	17	14	3.63E+05					NA
LU-04	US-COAL	420	536	0.6	1.5	12	1000	0.33	14	4.5	61	480.0	1523	1394	8	6	15						NA
LU-10	US-COAL	420	536	0.6	1.5	12	1004	0.33	13	6.5	160		1572	1347	14								NA
LU-04	US-COAL	420	536	0.6	2.0	12	1025	0.35	14	5.5	61	480.0	1497	1058	29	15	15						NA
LU-04	US-COAL	420	536	0.6	2.5	12	1000	0.33	14	5.5	160		1552	1067	31	15	15						NA
LU-04	US-COAL	420	536	0.6	3.0	12	1000	0.98		5.5	60	500.0	1652	994	40	13	15	7.03E+05					NA
LU-04	US-COAL	420	536	0.6	4.0	12	1045	0.98	12	7.0	98		1639	914	44	11							NA
LU-08	US-COAL	420	536	10.5	1.5	12	1017	0.34	14	4.3	60		1539	1271	17	11							NA
LU-08	US-COAL	420	536	10.5	2.0	12	1018	0.34	14	4.5	55		1537	1266	17	9	10						NA
LU-08	US-COAL	420	536	10.5	2.5	12	1002	0.32	13	5.3	71	500.0	1590	1115	30	12	11	4.30E+05					NA
LU-08	US-COAL	420	536	10.5	3.0	12	987	0.31	13	4.3	99		1530	1035	32	11	10						NA
LU-05	US-COAL	420	536	0.6	3.0	12	1029	0.35	13	5.5	60	540.0	1652	994	40	13	11	0.17E+06	5.6	1.1	15	2.4	81.12
LU-07	US-COAL	420	536	0.6	3.0	15	890	0.12	14	5.3	130	510.0	1575	997	37	12	13	2.20E+06					NA
LU-08	US-COAL	420	536	0.6	3.0	11	1200	0.60	14	5.0	65	500.0	1575	1102	30	10	10	1.40E+06	5.8	0.8	15	2.4	85.57
LU-14	US-COAL	420	536	0.6	3.0	10	1350	0.72	12	6.3	55		1730	1415	18	6							NA
LU-11	US-COAL	420	536	4.4	3.0	12	905	0.30	13	6.0	63		1580	954	37	13							NA
LU-15	US-COAL	420	536	4.4	3.0	11	1200	0.60	14	6.0	70		1464	1054	28	9							NA
LU-15	US-COAL	420	536	4.4	3.0	10	1313	0.72	14	6.5	70		1490	1131	24	8							NA
LU-15	US-COAL	420	536	4.4	3.0	12	964	0.28	14	6.7	150		1432	870	39	13							NA
LU-16	US-COAL	420	536	4.4	2.0	12	964	0.28	14	4.0	150		1536	1100	27	14							NA
LU-16	US-COAL	420	536	4.4	2.5	12	962	0.30	14	5.3	130		1575	1032	34	14							NA
LU-16	US-COAL	420	536	4.4	2.5	12	991	0.31	13	6.7	160		1600	1123	30	12							NA
LU-17	US-COAL	420	536	10.5	3.0	11	1367	0.72	14	6.0	130		1767	1200	29	10							NA
LU-18	US-COAL	420	536	4.4	3.0	12	1030	0.35	13	6.7	160		1611	971	48	13							NA
LU-20	US-COAL	420	536	10.5	3.0	10	1324	0.72	14	5.0	120		1575	1400	11	3							NA
LU-20	US-COAL	420	536	10.5	3.0	15	983	0.15	13	6.5	180		1572	1379	12	4							NA

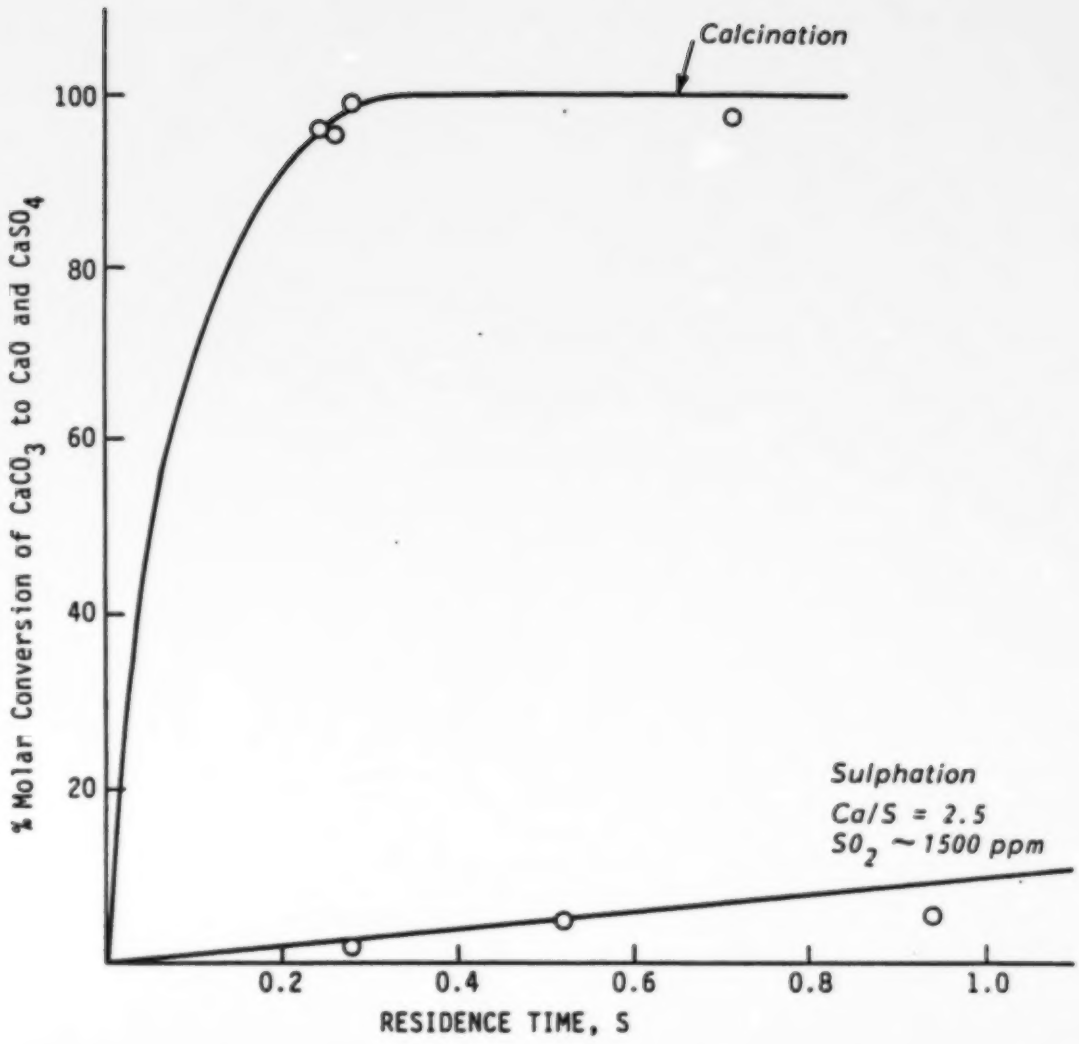


FIGURE 3-2
CALCINATION AND SULPHATION RATES

The development of surface area and porosity of the calcine appears to be very sensitive to the temperature at the injection location, as shown in Figure 3-3. The data indicate that the calcine has higher porosity and more surface area than the parent stone even at the highest, most unfavourable injection temperature. Surface area increases from 1.3 to 3.6 m^2/g and porosity from 17 to 25% after calcination at 1200°C. Both properties continue to increase with decreasing injection temperatures. At around 1000°C (wall temperature) the surface area of the calcine is 11.6 m^2/g and porosity is 48%. No data are available for temperatures lower than 1000°C, but the plots indicate that development of both surface area and porosity slows down at around 1000°C.

In Figure 3-4 the reactivity of the stone in terms of its sulphur capture potential is plotted vs calcine surface area. Stone reactivity increases with increasing surface area, and approaches an asymptotic value of approximately 50% SO_2 capture at the highest surface area and porosity measured under the conditions of these tests. (Ca/S mole ratio = 2.5, SO_2 in flue gas ~ 1500 ppm and furnace quenching rate = 536°C/S). These results indeed show that reactivity is closely related to surface area, the development of which is greatly affected by injection temperature.

The plot in Figure 3-5 correlates SO_2 capture with injection temperature (wall temperature). Temperature at the injection location I_2 ~ 1000°C appears to be the optimum for maximum sulphur capture. As expected from the porosity and surface development of the stone in the furnace, reactivity drops sharply with increasing temperature due to the drop in porosity and surface area associated probably with sintering and dead-burning. At the low temperature end of the plot decreasing sulphur capture is probably due to lower rates of sulphation and shorter residence time in the furnace.

3.2 Coal Firing - Effect of Operating Variables

This section of the report discusses the results obtained with coal firing. A high volatile bituminous coal with 1.7% sulphur was fed into the furnace under conditions described in Section 2.3(b). A Beachville limestone was used in this phase of the study and the effect of operating variables on SO_2 capture and sorbent utilization (ie injection temperature, residence time, sorbent addition rate and particle size) were studied and optimized. The ash from the process was also characterized for optimized operating conditions and the performance of the ESP under increased ash loading was determined. The accumulation of ash in the furnace and heat exchangers and its effect on system operation were also evaluated. The results of these tests are summarized in Table 3-2.

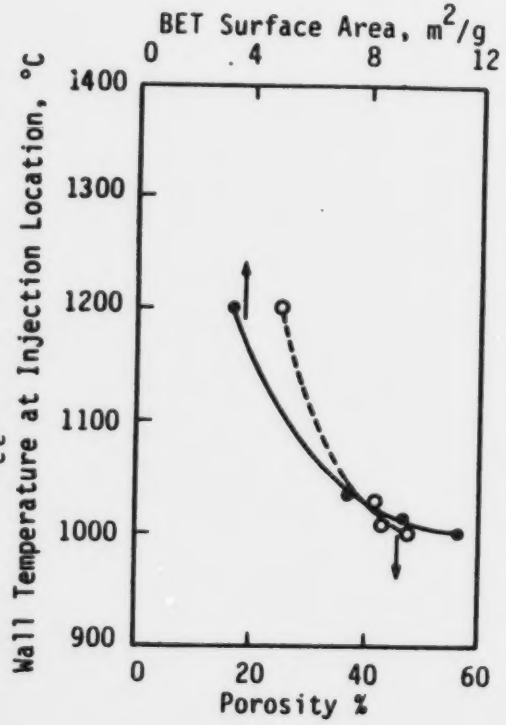


FIGURE 3-3

DEVELOPMENT OF CALCINE POROSITY AND SURFACE AREA

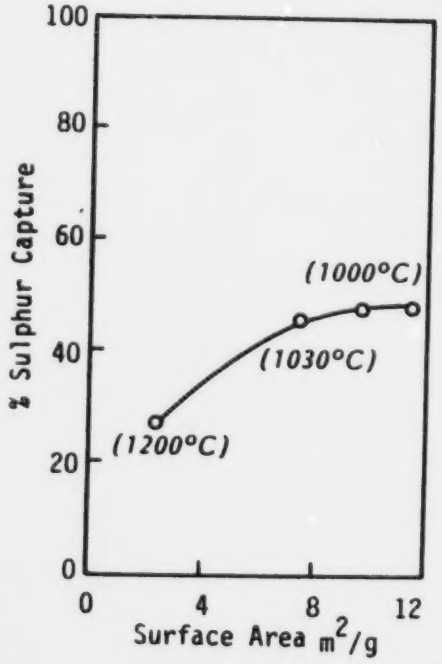


FIGURE 3-4

REACTIVITY VS SURFACE AREA

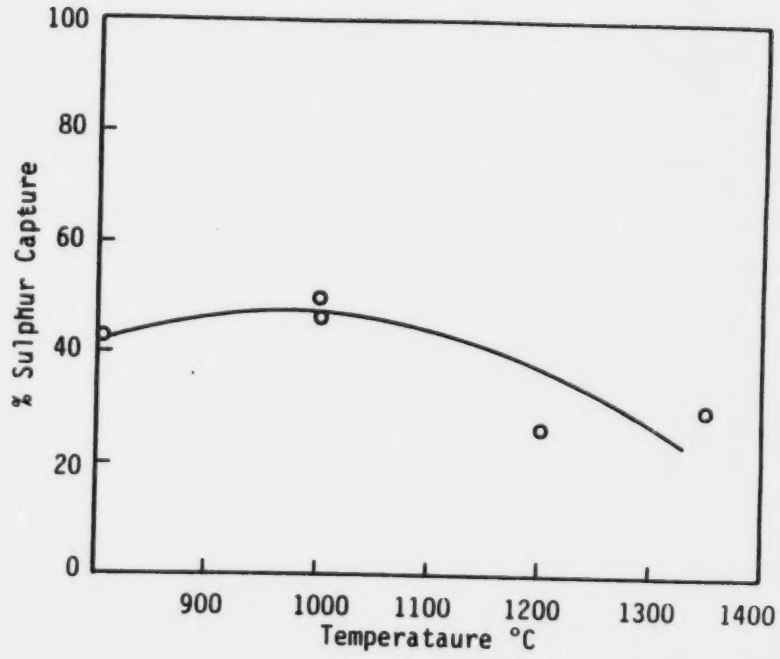


FIGURE 3-5

SULPHUR CAPTURE VS INJECTION TEMPERATURE

Beachville Limestone, MMD 8.6 µm, Porosity 17%, Surface Area 1.3m^2/g
Propane Firing
Furnace Quenching Rate 536°C/s
Limestone Addition Rate Ca/S Ratio = 2.5

(a) Effect of Injection Temperature

To study the effect of injection temperature on sulphur capture, limestone with MMD = 4.4, 8.6 and 10.5 μm's were injected into the furnace at a Ca/S mole ratio = 3 at injection sites I_0, I_1, I_2 and I_3 at which the wall temperatures are approximately 1350, 1200, 1000 and 850°C respectively. SO_2 content of the flue gas was monitored before and after limestone injection when the system reached steady-state conditions. SO_2 levels in table 3-2 are normalized to 5% O_2 in the flue gas. SO_2 capture as a function of injection temperature are plotted in Fig 3-6 under the above specified operating conditions. The equation that fits the data best having a correlaton coefficient of 0.91 (ie. $R^2 = 0.83$) is given below:

$$S\ Capture, \% = a_0 + a_1S + a_2T + a_{11}S^2 + a_{12}ST + a_{22}T^2$$

where the constants

a_0 = -199.31
a_1 = 9.67
a_2 = 0.408229
a_{11} = -0.92
a_{12} = 0.00213333
a_{22} = -0.000203493 and
S = particle size, μm
T = temperature, °C

The low SO_2 capture observed at 1200°C in Figure 3-6 probably indicates that the decrease in sulphur capture with increasing temperatures between 1000 and 1200°C is sharper than indicated by the empirical curve. Future bench scale tests will address this problem.

For comparison SO_2 capture by limestone from an SO_2 doped flue gas under similar operating conditions is also shown. The plots indicate that the optimum injection temperature is around 1000°C for both cases. At this temperature about 50% SO_2 is removed from SO_2 doped gas stream and about 40% from flue gases from coal-firing.

SO_2 removal efficiency drops to much lower levels at higher injection temperatures. This reflects the loss of limestone reactivity at those temperatures where calcine surface area and porosity are much lower than at optimum temperature. SO_2 capture also decreases at the low temperature end of the plot, probably because of the slower rate of reaction between SO_2 and calcine at these temperatures. The shorter residence time available in the reaction zone, when the limestone is injected at the bottom of the furnace is also likely to contribute to this. The lower SO_2 capture in coal-fired systems as compared to gas-firing probably indicates that there is some interaction

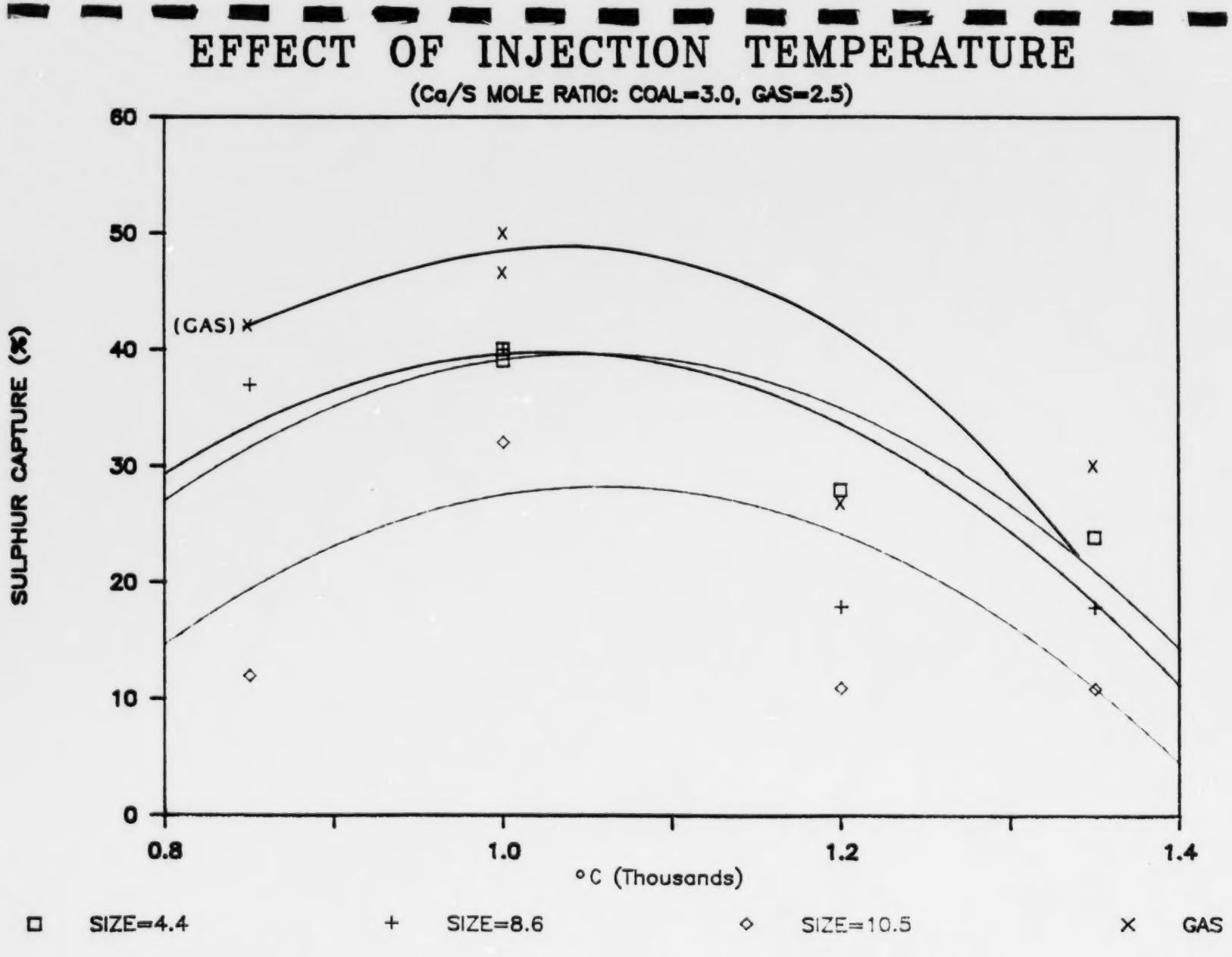


FIGURE 3-6

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between limestone and ash particles which results in decreased reactivity. This is an area which will have to be explored further.

(b) Effect of Sorbent Addition Rate

The effect of sorbent addition rates on sulphur capture and sorbent utilization were evaluated for limestone with MMD = 10.5, 8.6 and 4.4 microns. Limestone was injected at the optimum injection temperature (~1000°C) at I_2.

Percentage sulphur capture as a function of Ca/S ratios are plotted in Figure 3-7. These plots show an increased SO_2 capture with increased sorbent addition rate up to about Ca/S ratio = 2.5-3.0. Beyond this, SO_2 capture begins to level off. % SO_2 removal is best represented by the equation below:

$$S\ Capture,\ \% = a_0+a_1S+a_2e^{-1.5R}+a_{11}S^2+a_{12}Se^{-1.5R}+a_{22}e^{-3R}$$

where the constants

a_0 = 22.584
a_1 = 7.9498
a_2 = -632.88
a_{11} = -0.63622
a_{12} = 30.980
a_{22} = 752.028
S = particle size, µm
R = Ca/S mole ratio

The multiple correlation coefficient for these plots was found to be 0.99 (ie. R^2 = 0.89).

The effect of sorbent addition rate on sorbent utilization is shown in Figure 3-8, for the set of conditions specified above. There is a considerable spread in these data. The general trend however, indicates that at higher than 2.5-3.0 Ca/S ratios sorbent utilization drops significantly.

Under optimum operating conditions, injection temperature ~1000°C, sorbent particle size 8.6 µm, SO_2 capture is about 40% and sorbent utilization is between 13 and 14%.

(c) Effect of Sorbent Particle Size

These tests were designed to evaluate the effect of limestone particle size on SO_2 capture. Three limestone samples with MMD 10.5, 8.6 and 4.4 µm were used in the study. A very fine grind, 100% passing 20 µm screen was also tried. Great difficulties were experienced in feeding the fine material, as the particles agglomerated in the feeding pipe and plugged it. To overcome this difficulty the fine material was blended with the 8.6 µm

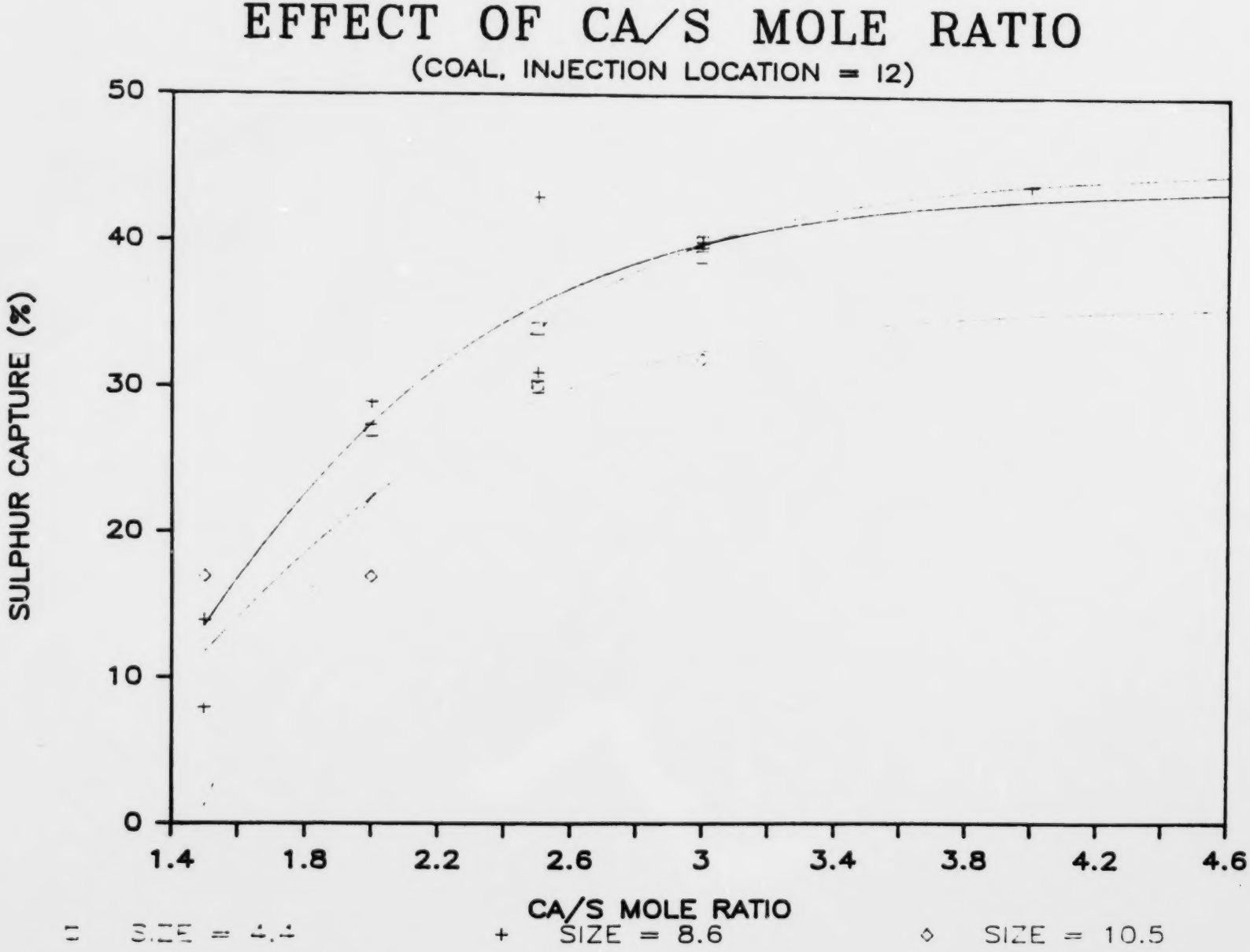

FIGURE 3-7

170769 RI

EFFECT OF CA/S MOLE RATIO

(COAL, INJECTION LOCATION = 12)

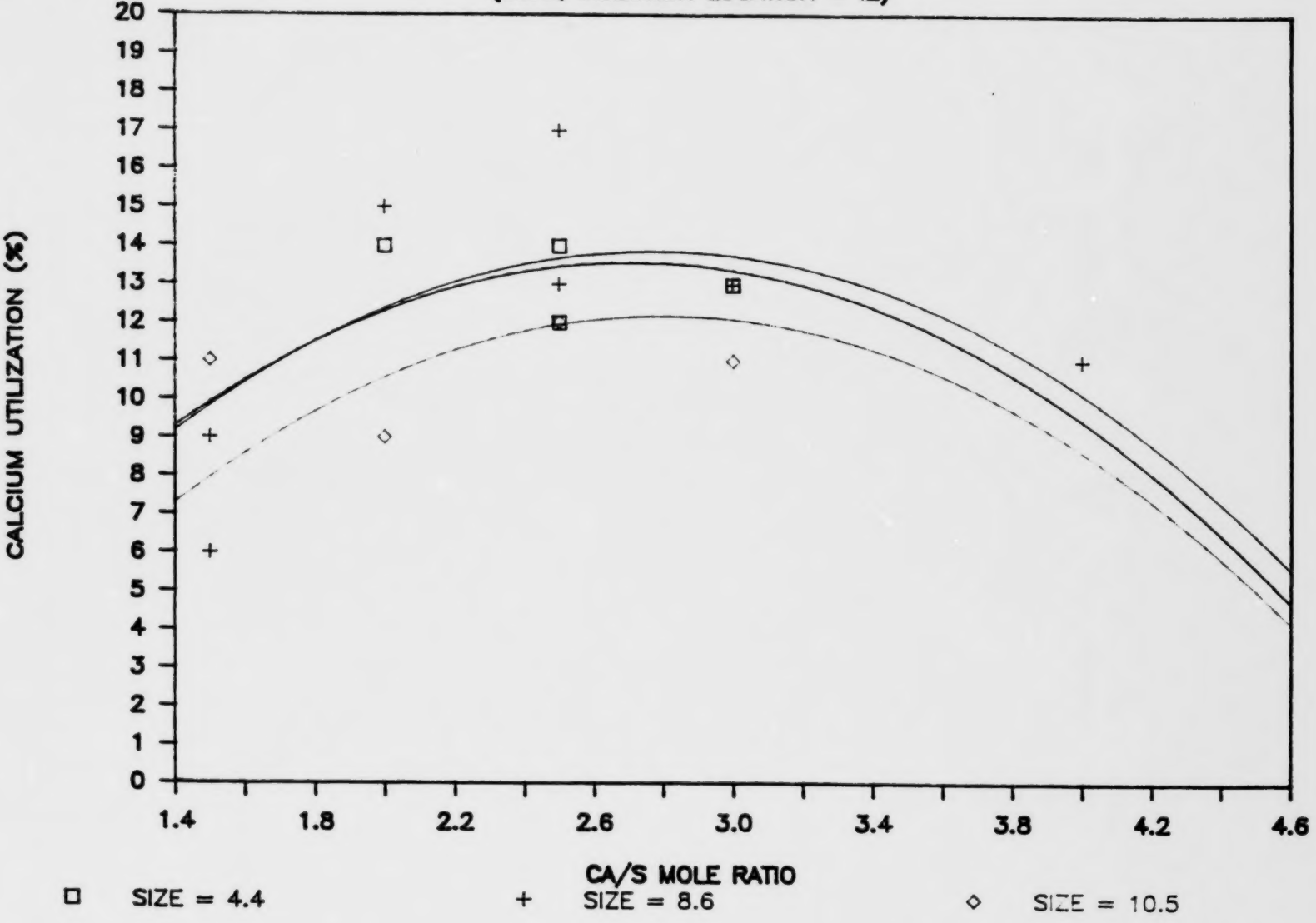

FIGURE 3-8

170763 RD

limestone. The mass median diameter of this blend was 4.4 μm and it was fed successfully. The particle size distribution of the various blends tested are given in Table 2-4 and Fig. 2-9.

The SO_2 capture as a function of limestone particle size at Ca/S ratios ranging from 2 to 3, at injection location I_2, (~1000°C) are given in figure 3-9. The results indicate that sulphur capture improves by decreasing limestone particle size from 10.5 to 8.6 μm. Further decrease in particle size results in slightly reduced SO_2 removal, probably because of the blinding of very fine particles.

The equation that best represents this fit and having a correlation coefficient of 0.99 (ie. $R^2 = 0.89$) is given by:

$$\text{S Capture, \%} = a_0+a_1S+a_2e^{-1.5R}+a_{11}S^2+a_{12}Se^{-1.5R}+a_{22}e^{-3R}$$

where
$a_0 = 22.584$
$a_1 = 7.9498$
$a_2 = -632.88$
$a_{11} = -0.63622$
$a_{12} = 30.980$
$a_{22} = 752.028$ and
S = particle size, μm
R = Ca/S mole ratio

(d) Effect of Residence Time

The influence on SO_2 capture of the residence time in the sulphation zone, where temperature ranges between T_I-850°C (T_I is the temperature at injection location I) was studied by injecting limestone into the furnace at various locations, thereby providing various residence times for the sulphation reaction. The results of these tests are plotted in fig 3-10. Residence times were varied between 0.12 to 0.72 seconds depending on the injection site. Longer residence times did not result in higher SO_2 capture because at the same time injection temperatures were higer. Under optimized operating conditions (ca/S = 3.0, particle size = 8.6 μm and T~1000°C) maximum SO_2 capture was achieved within 0.3 to 0.5 sec. The wall temperatures are shown in brackets at the various injection sites. The shape of this figure is similar to that of SO_2 capture vs temperature at the injection sites (see Figure 3-6), suggesting that the effect of residence time is masked by the effect of temperature.

This can be understood since changing the injection location affects both temperature and residence time. The effect of these variables on SO_2 capture could not be decoupled in this phase of the study, because the quenching rate was not varied.

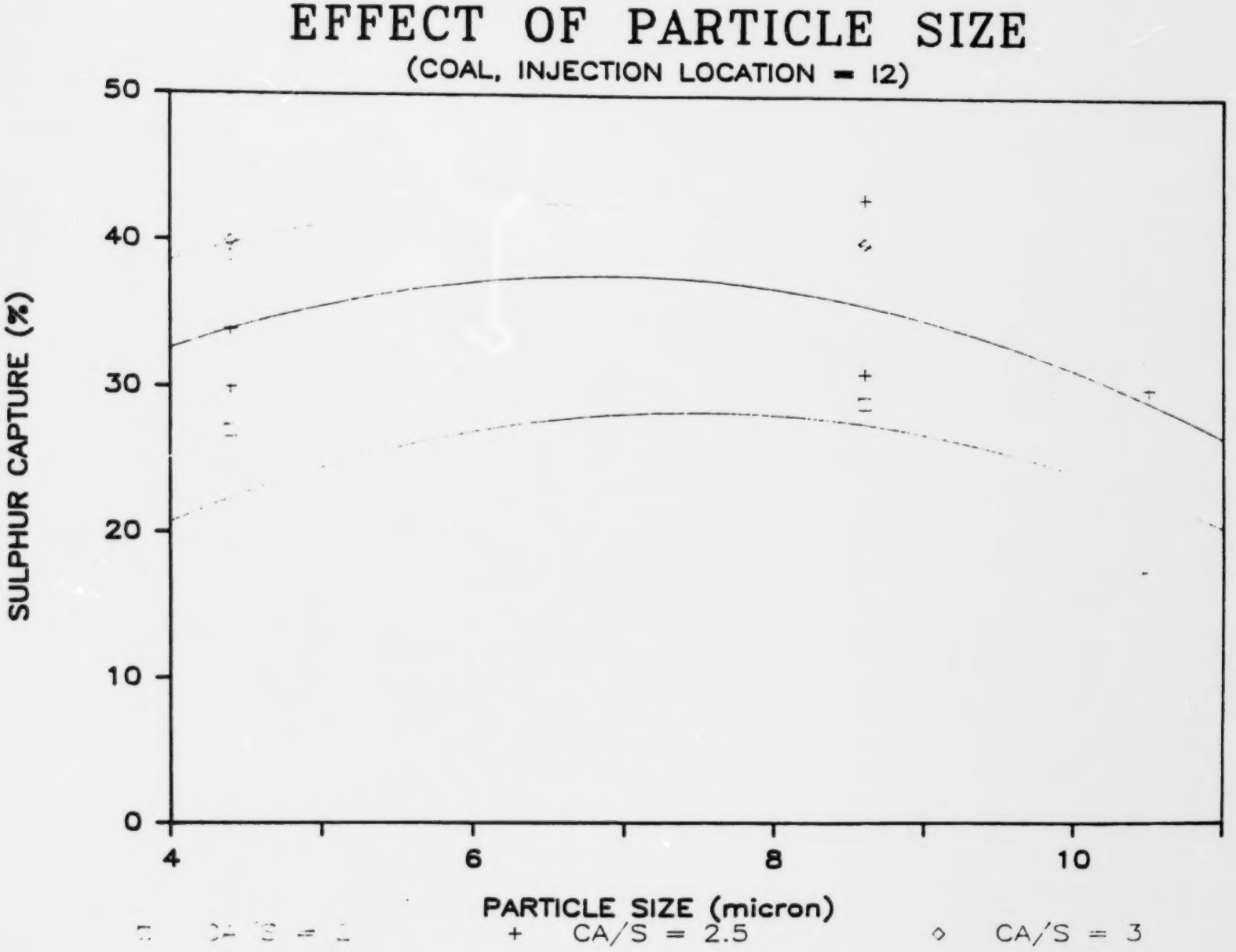

FIGURE 3-9

170765 RD

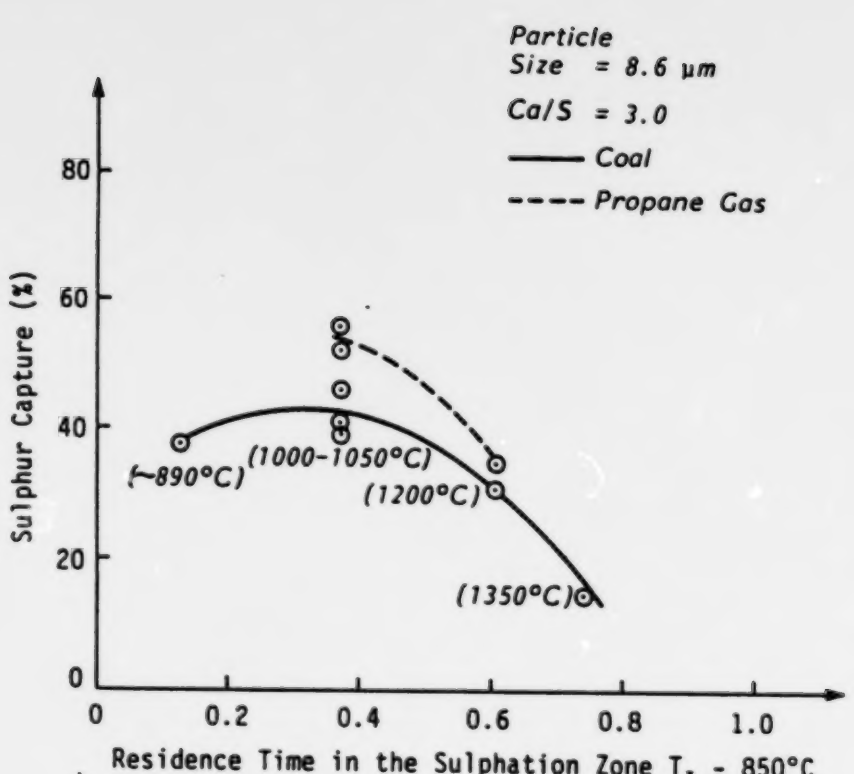

FIGURE 3-10
EFFECT OF RESIDENCE TIME

In the next phase of the study the sulphation zone temperature-time history will be varied by changing furnace quenching rates. This will permit the decoupling of these variables and hence the residence time effect should become clear.

(e) Response Surface Diagrams

Figures 3-11 to 3-16 are the response surface diagrams relating sulphur capture and calcium utilization to process variables. For an explanation of the development of the response surfaces see Appendix I. Figure 3-11 shows the three dimensional response relating sulphur capture to injection temperature and sorbent particle size at constant Ca/S mole ratio 3. Figure 3-12 is the corresponding two dimensional contour. Similarly, Figures 3-13 and 3-14 are the three dimensional and two dimensional responses of sulphur capture versus sorbent particle size and Ca/S mole ratio at injection temperature ~ 1000°C. Figures 3-15 and 3-16 depicts the calcium utilization response as a function of particle size and Ca/S mole ratio at constant injection temperature ~ 1000°C. Interpretation of the three dimensional surfaces can become a somewhat tedious procedure, hence the two dimensional contours are more realistic to visualize. For example, take Figure 3-12 which shows the sulphur capture response as a function of injection temperature and particle size. At an injection temperature of 1000°C and particle size 8.6 μm, the response surfaces predict a sulphur capture of approximately 38%. This compares well with 40% SO_2 removal observed for the same conditions.

3.3 Effect of Limestone Injection on Fly Ash Characteristics and ESP Performance

Ontario Hydro boilers, which are candidates for SO_2 control using limestone injection are equipped with electrostatic precipitators. For limestone injection to be competitive as a cost effective SO_2 control option, problems of particulate collection in the ESP must be overcome. ESP performance is reduced both by substantial increases in particulate loading and by an increase in resistivity. Potential solutions to restore ESP performance include: enlarging the ESP, using pulse energization, flue gas humidification or using chemical conditioning.

In this phase of the program the effect of furnace sorbent injection on the properties of ash/sorbent mixture (chemical composition, particle size distribution, fusibility and electrical resistivity), ash loading and their effect on ESP performance have been studied. In the next phase humidification to condition the ash will be investigated.

SULPHUR CAPTURE RESPONSE SURFACE

(Ca/S MOL.RATIO = 3.0)

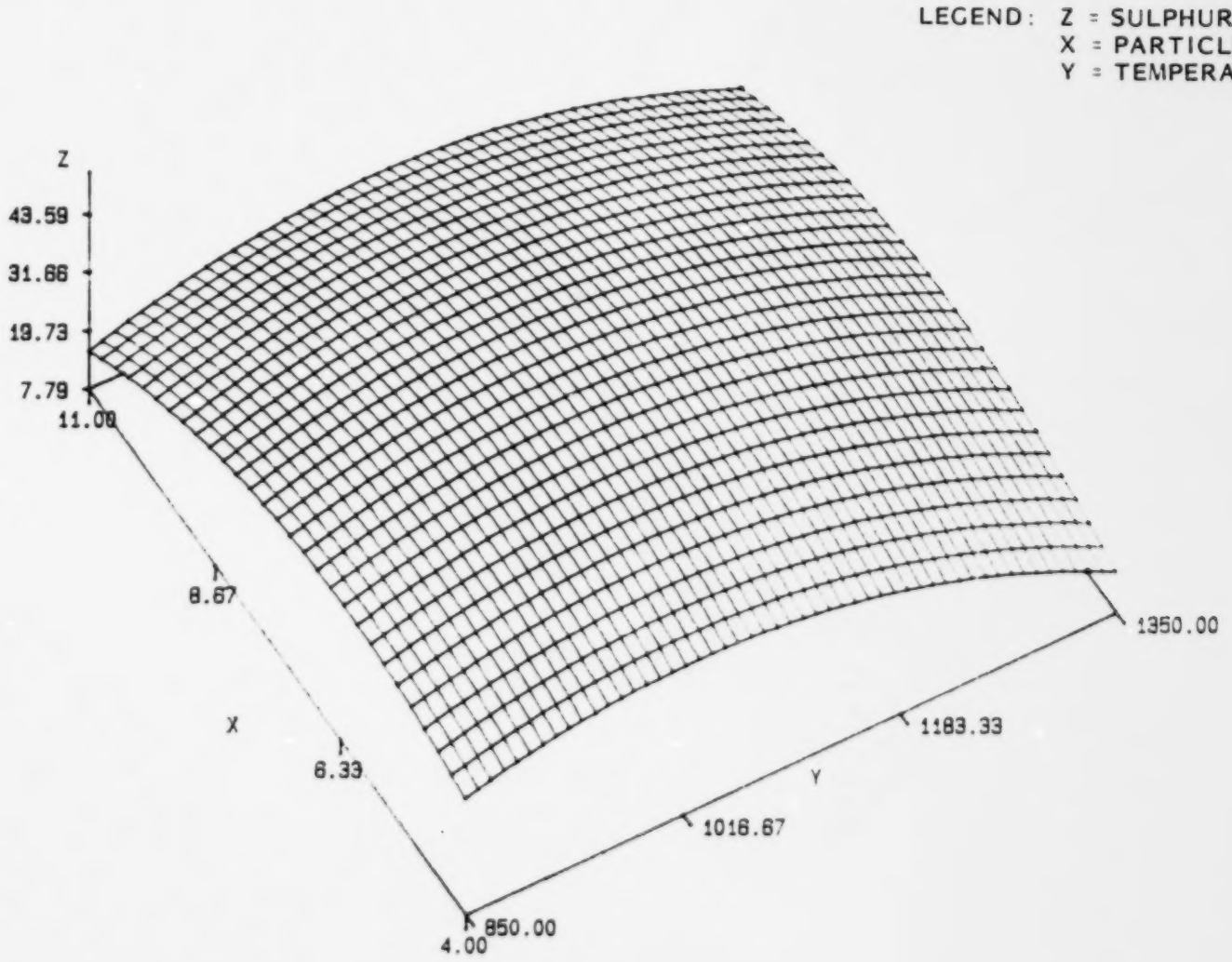

FIGURE 3-11

SULPHUR CAPTURE RESPONSE SURFACE

Z = SULPHUR CAPTURE (%) X = PART. SIZE Y = TEMPERATURE

(Ca/S MOL. RATIO = 3.0)

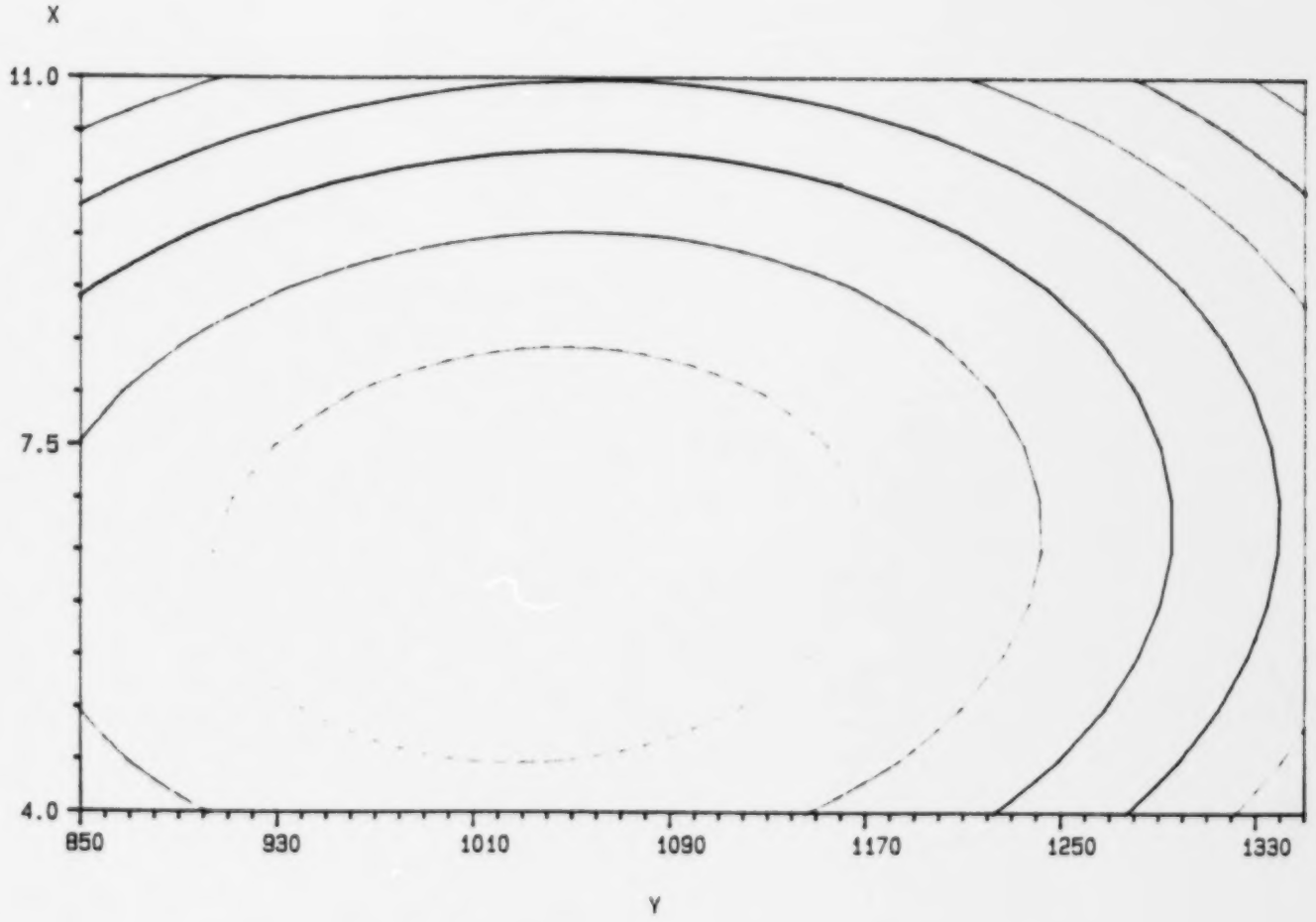

FIGURE 3-12

SULPHUR CAPTURE RESPONSE SURFACE

(INJECTION TEMP. ~1000°C)

LEGEND: Z = SULPHUR CAPTURE, %
X = PARTICLE SIZE, μm
Y = Ca/S MOL. RATIO

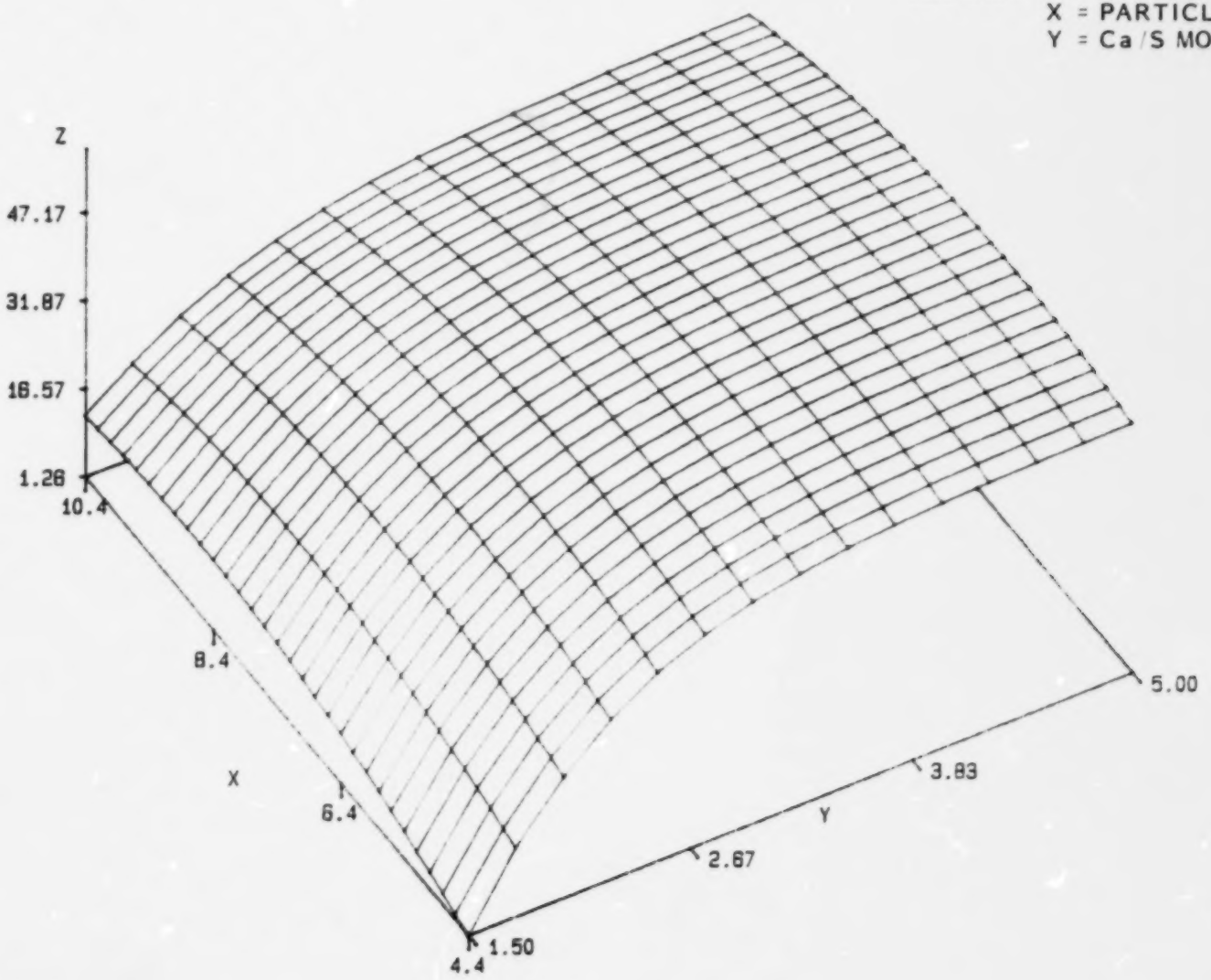

FIGURE 3-13

SULPHUR CAPTURE RESPONSE SURFACE

Z = SULPHUR CAPTURE (%) X = PART. SIZE Y = CA/S MOL.RT

(INJECTION TEMP. -1000°C)

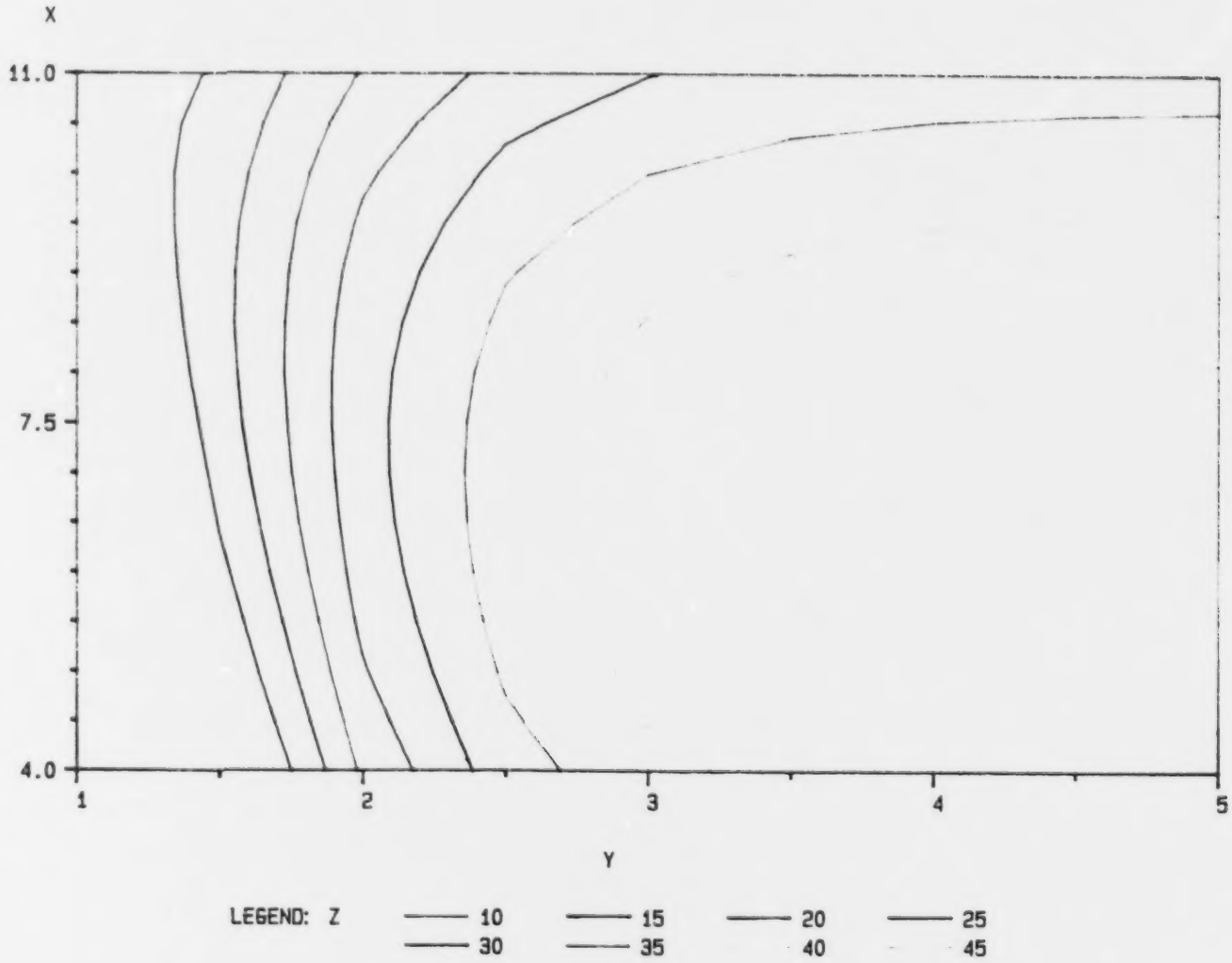

FIGURE 3-14

CALCIUM UTILIZATION RESPONSE SURFACE

(INJECTION TEMP. -1000°C)

LEGEND: Z = CALCIUM UTILIZATION, %
X = PARTICLE SIZE, μm
Y = Ca/S MOL.RATIO

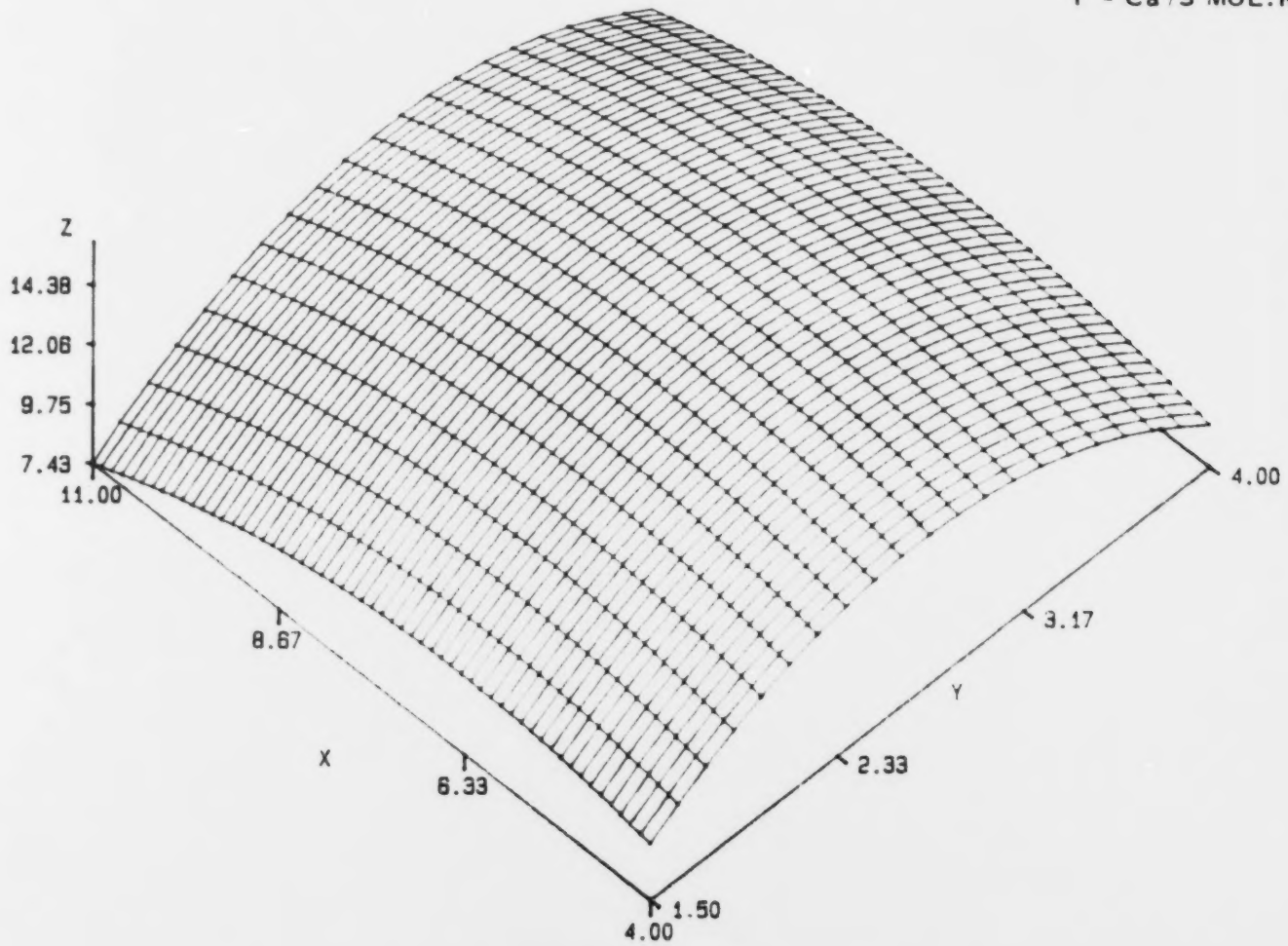

FIGURE 3-15

CALCIUM UTILIZATION RESPONSE SURFACE

Z = CALCIUM UTILZATION (%) X = PART.SIZE Y = CA/S MOL.RT

(INJECTION TEMP. ~1000°C)

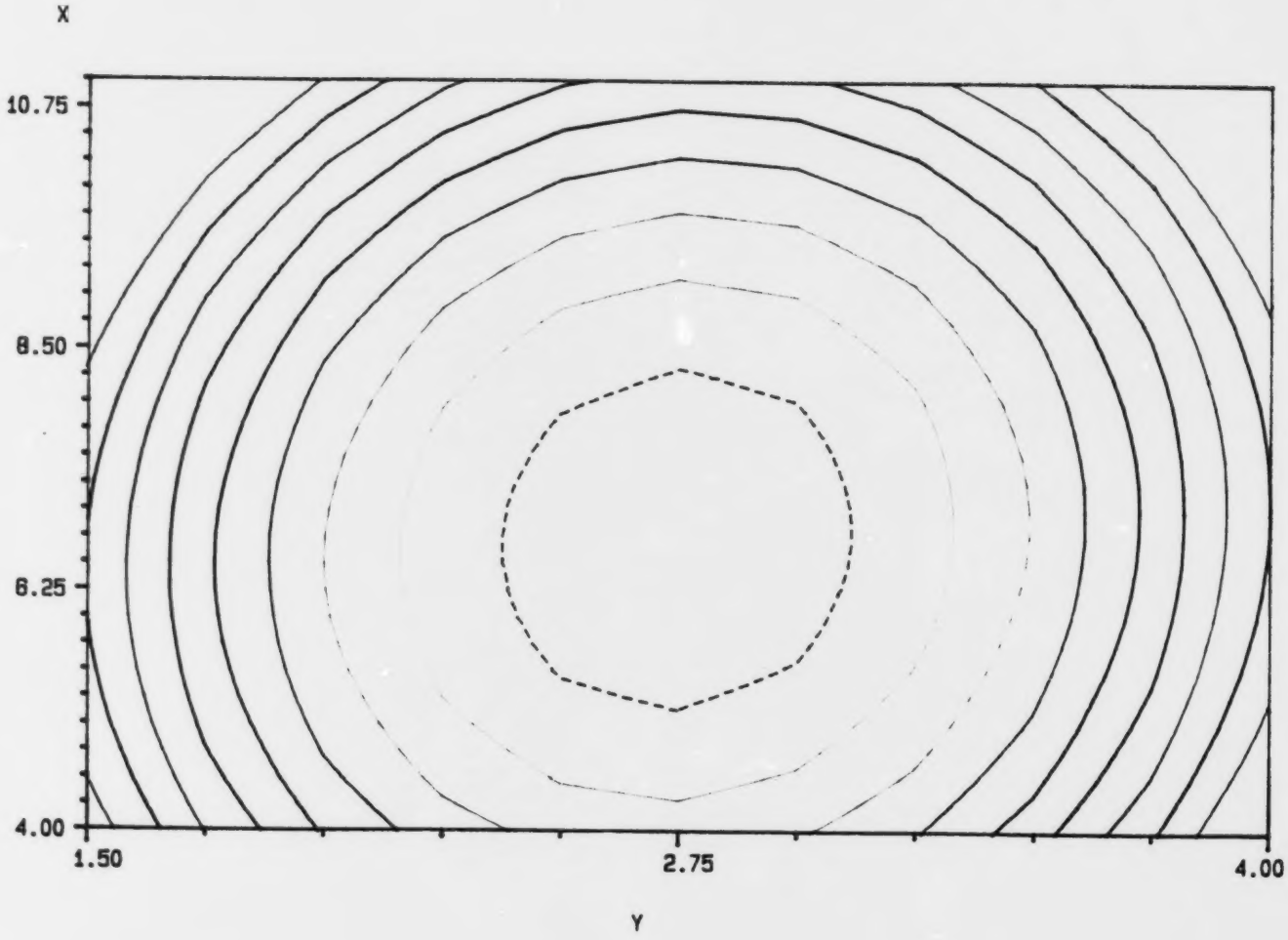

FIGURE 3-16

To determine if the CRF produced fly ash similar to that obtained during full scale burns at Lakeview TGS, a comparison was made between the two. The comparison shown in Table 2-3 and Figure 2-8 of section 2.2(e) indicates that the properties of the ashes resulting from burning a medium sulphur high volatile bituminous coal are very similar.

(a) Ash Properties and Carbon Burnout

Laboratory and in situ ash characterization were performed as described in section 2.2(e) on ash/sorbent mixtures while burning a high volatile U.S. bituminous coal at the CRF.

Comparison between chemical composition, particle size distribution and ash fusion temperatures of ashes produced at the CRF with and without limestone addition are given in Table 3-3. In Table 3-4 calcium oxide, sulphate and carbonate content of the ashes are shown. Electrical resistivity, dust loading before and after the ESP and precipitator performance for runs with the best removal efficiences are also shown. These results are compared to ashes collected at Lakeview TGS during the limestone injection test program/13/. The table also includes the analysis of a typical Consol waste/14/.

The particle size distribution of CRF baseline and limestone injection ashes is shown in Figure 3-17. The data indicate that the limestone injection ash is finer than the baseline ash: 80% of the limestone injection ash is less than 24 μm compared to 36 μm for the baseline ash. This is likely to affect ESP performance.

The limestone injection waste contains high levels of CaO and $CaSO_4$. CaO content of typical ashes ranges between 226 to 337 g/kg and $CaSO_4$ between 136 to 150 g/kg, depending on the front end conditions such as Ca/S mole ratio and sulphur capture. The waste also contains $CaCO_3$, the presence of which can probably be attributed to the reacton between CaO in the ash and CO_2 in the flue gas. This suggestion is based on the calcination data discussed in Section 3.1 which indicated 99.5% decomposition of $CaCO_3$ to CaO in less than 300 ms in the furnace.

It is important to note that the calculated composition of limestone injection wastes compare well with the analysis (see Appendix II for sample calculation).

CaO and $CaSO_4$ content of Lakeview TGS ashes appear to be somewhat lower than expected on the basis of material balances. This is probably due to the fact that the samples analyzed are composite samples from the hoppers and do not necessarily

Table 3-3
COMPARISON BETWEEN BASELINE AND LIMESTONE INJECTION ASH FROM THE CRF

Particle Size Distribution of the Ash

Sieve Opening µm	Cumulative % Undersize	
	* Baseline Ash	**Limestone Injection Ash
7	10	13
17	54	74
37	60	92
44	92	94
75	96	99
105	98	100
250	100	

Chemical Composition, g/kg

	*Baseline Ash (CRF)	Limestone Injection Ash (CRF)	
Na_2O	6	† 3	** 3
K_2O	17	7	9
MgO	9	10	12
CaO	50	334	416
Fe_2O_3	77	38	50
Al_2O_3	215	110	106
SiO_2	451	225	215
SO_3	23	80	88
LOI	161	143	108

Ash-Fusion Temperature, °C
Reducing Atmosphere

	Baseline Ash* (CRF)	Limestone Injection Ash (CRF) †
Initial Deformation Temp, IT	1240	1380
Softening Temp, ST	1270	1400
Hemispherical Temp, HT	1290	1405
Fluid Temp, FT	-	1410

Run No
* LV - 02
** LV - 06 Ca/S = 3.0, SO_2 capture = 40%
† LV - 01 Ca/S = 2.5, SO_2 capture = 43%

Table 3-4

Comparison of CRF, Lakeview TGS and Consol Wastes

Waste Material	Limestone Injection Parameters		Waste Composition g/kg						Kg Waste/100 kg Coal (estimated)	Ash Resistivity ohm. cm	Dust Loading, g/m³		* ESP Performan
	Ca/S ratio	% SO_2 removal	CaO	$CaSO_4$	$CaCO_3$	Loss on Ignition	Carbon in Ash as is	Carbon in Ash on sorbent free basis			Before ESP	After ESP	
CRF Baseline Ash			34	39		161 147			8.8	2.0×10^5 5.1×10^5	3.4 3.2	0.26 0.26	90 92
Limestone Injection Wastes													
CRF - LV - 01	2.5	43	226	136	90	143	103	~185	~16	3.6×10^5			
- LV - 04	3.0	40				147				7.8×10^5			
- LV - 05	2.5	30				107				4.3×10^5			
- LV - 06	3.0	40	337	150	30	108	95	~204	~18	8.2×10^6	5.6	1.1	81
- LV - 07	3.0	37				134				2.2×10^6			
- LV - 08	3.0	30				101				1.5×10^6	5.6	0.83	86
Lakeview TGS - Unit 4-2001-w - Dec 10, 1985 Composite Sample from East-West Hoppers /13/	3.1	43	265	111	48		101	~175	~15				
- Dec 12, 1985 Composite Sample from East-West Hoppers	2.7	40	284	118	55		89	~160	~16				
Consol Waste /14/			333	182	80		129	~318					

* Electric field ---- ~2.4 kV/cm
specific collection area (SCA) ~15 $m^2/m^3/s$

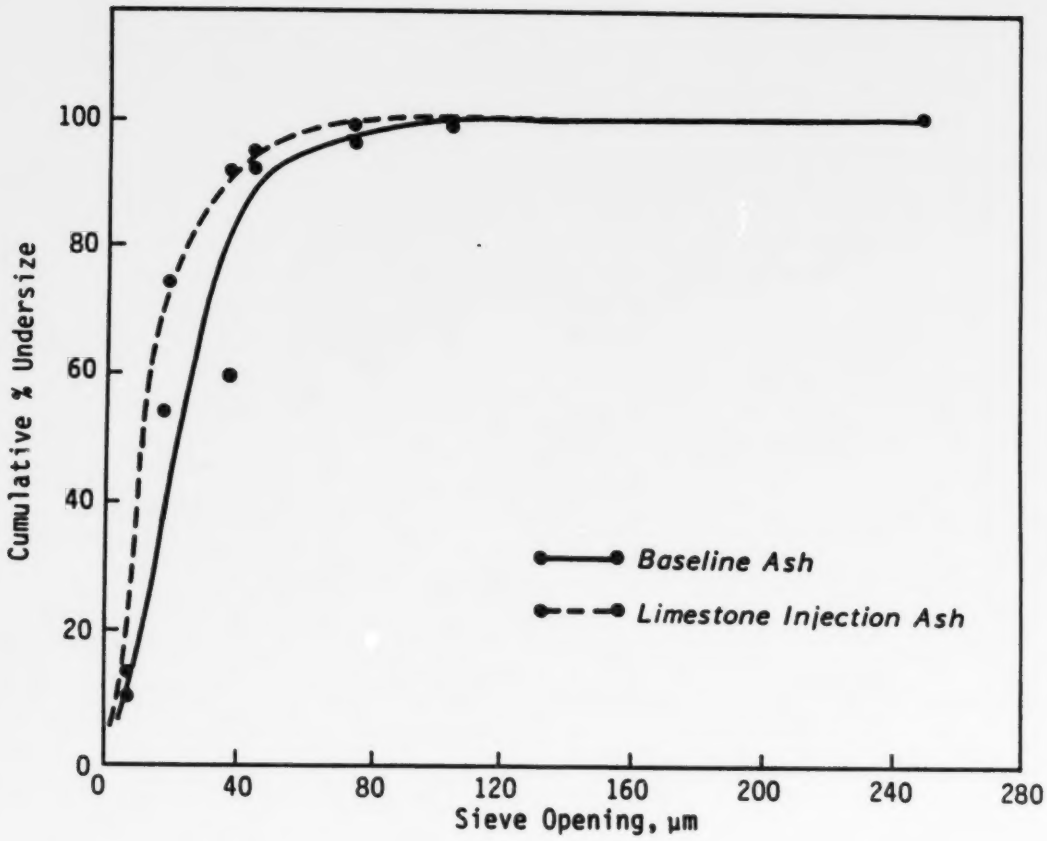

FIGURE 3-17

COMPARISON OF BASELINE AND LIMESTONE INJECTION ASH AT THE CRF

represent the ashes for the front end conditions specified in Table 3-4. Composition of Consol ash is similar to the CRF ash except for its higher carbon levels.

The limestone injection process produces approximately 2 times more waste than the baseline ash. The larger quantities of a finer waste with high calcium oxide levels is expected to pose problems on waste handling and disposal and collectability by ESP.

Carbon content of CRF and Lakeview TGS limestone injection wastes are similar, ranging between 89 to 103 g/kg ash. Carbon levels of CRF waste on a sorbent free basis are higher than that of the baseline ash, 185 to 206 vs 141 to 160 g/kg. The estimated heat losses, due to the higher levels of carbon in the limestone injection ash is about 1.1% as compared to 0.7% for the baseline ash (see Appendix III). Carbon on a sorbent free basis of Lakeview TGS ashes is somewhat lower than that of CRF, because of the lower CaO and $CaSO_4$ levels found in these. When more accurate data will become available a better comparison could then be made.

(b) Dust Loading and ESP Performance

Limestone injection to the furnace resulted in an elevated dust loading to the ESP from 3.3 (base-line ash) to 5.6 g/m^3. This represents a load increase by a factor of 1.7. It must be pointed out however, that significant amounts of waste was found deposited on the heat exchangers, indicating that not all the waste was entrained in the flue gas. It is possible that dust loading to the precipitator could be even higher than measured in these tests. Dust loading after the ESP was 3 to 4 times higher than in the case of baseline ash.

The resistivity of the baseline ash was found to be low 2.5×10^5 ohm·cm, while that due to limestone injection was higher by one half to one order of magnitude ranging between 0.36 to 8.2×10^6 ohm·cm. The low resistivities measured probably can be attributed to the relatively high carbon levels in the ash found under conditions simulating Lakeview TGS high quenching rates. Under these conditions the resistivities are well within the range where good precipitator performance is expected.

The precipitator with a specific collection area (SCA) of $15 m^2/m^3/S$ and electric field strength of 2.4 kv/cm collected the limestone injection waste with an efficiency of 81 to 85%. This efficiency is significantly lower than the efficiency with which the base-line ash was collected (90-92%). The observed impaired precipitator performance is probably due to the high dust

loading and finer dust rather than due to increased ash resistivities.

(c) Slagging and Fouling Propensities of the Waste

Although particulate loading to the ESP increased significantly no slagging was observed in the furnace. Soft deposits which form at low temperatures and are generally characteristic of deposits found on air heaters and economizers were observed on the furnace walls and heat exchanger surfaces. These deposits could be easily blown away by compressed air suggesting that conventional soot blowing equipment may suffice for full scale boiler injection of limestone. It is worthwhile to point out that during the test runs it was suspected that some lime could selectively deposit on the heat exchanger surfaces. Analysis of samples collected from a clean surface and one contaminated from a previous run, however, showed no selective precipitation. One observation made that could be of interest is that deposition of particles on the surfaces of the heat exchangers during limestone injection impaired their heat transfer rates markedly.

Reference to Table 3-3 which in part summarizes the ash fusibilities of the baseline and limestone injection ashes compares the ash fusion temperatures of both ashes. Although the melting temperature of the baseline ash was not recorded it is assumed to be very close to 1290°C as the transition from hemispherical to fluid temperature is very rapid. The fluid temperature of the limestone injection ash was recorded as 1410°C. This indicates that the baseline ash has the potential to slag more readily than the limestone injection ash.

4.0 SUMMARY

The effect of operating variables on sulphur capture by limestone injection into the furnace has been studied at Ontario Hydro's 620 MJ/h combustion research facility, under conditions simulating Lakeview TGS quenching rate. A highly volatile, 1.7% sulphur eastern U.S. bituminous coal and a non-porous limestone from Beachville, Ontario have been used in the study.

Rates of calcination and sulphation were estimated while burning propane gas and physical properties of the calcine such as porosity and surface area were correlated with the reactivity of the stone. The effects of injection temperature, residence time, limestone particle size and sorbent addition rate have been optimized for maximum SO_2 capture and sorbent utilization.

Chemical composition, carbon content and resistivity of ashes for runs with high SO_2 removal efficiency were determined. Dust loading, ESP performance and slagging and fouling properties of selected ashes were compared to that of the baseline ash.

The results of the study can be summarized as follows:

Calcination of Beachville limestone in a propane gas flame is complete within less than 300 ms when injected into the furnace at ~1000°C.

Sulphation indicated by tests conducted in an SO_2 doped propane gas flame is much slower than calcination and is the rate determining step in the process.

Surface area, porosity and reactivity increase with decreasing reaction temperatures in the temperature range between 1200 to 1000°C. At about 1000°C porosity and surface area peak and reactivity is the best.

SO_2 capture is a very sensitive function of furnace temperature, which is determined by location of limestone injection ports. Optimum wall temperature at the injection site was found to be about 1000°C. This wall temperature corresponds to about 1100°C at the centre of the furnace.

SO_2 capture increases slightly with decreasing limestone particle size in the range betwen 10.5 to 8.6 μm. Further size reduction results in decreased SO_2 removal, probably due to higher potential for surface blinding in the case of very fine particles.

SO_2 removal efficiency and sorbent utilization are improved with increasing sorbent addition rate up to a Ca/S ratio of 3. Further increase does not improve SO_2 capture and drastically reduces sorbent utilization.

The effect of residence time could not be determined in the study, since both furnace temperature and residence times are determined by the location of limestone injection sites. Under optimized operating conditions maximum sulphur capture can be achieved within 0.3 to 0.5 s. The effect of temperature is suspected of masking the effect of residence time. Changing the time-temperature history in the furnace in the next phase of the study will decouple these effects.

Response surface diagrams have been developed to correlate sulphur capture and sorbent utilization with the most

important operating variables such as injection temperature, sorbent addition rate and particle size. These diagrams are useful for predicting SO_2 removal efficiencies and sorbent utilization for various operating conditions.

The process produces about 2.2 times as much ash as the baseline coal. The limestone injection ash is finer than the coal ash and contains higher levels of carbon on a sorbent free basis. It is estimated that as a result of this about 1.1% of the input heat is lost in the ash as compared to 0.7% in the baseline ash.

CaO and $CaSO_4$ content of the ash ranges between 226-337 g/kg, depending on sorbent addition rate and sulphur capture. A small amount of $CaCO_3$ was also found in the ash probably due to the recombination of CO_2 in the flue gas and unreacted CaO.

Dust loading to the ESP increased by a factor of 1.7. Dust loading after the ESP was found to be about three times higher than in the case of the baseline ash. The resistivity increased by one half to one order of magnitude to a maximum of 8.2×10^6 ohm cm. These low resistivities can probably be attributed to the relatively high carbon concentration in the ash.

The precipitator with a SCA of 15 $m^2/m^3/S$ collected the limestone injection waste with an efficiency of 81 to 85%. This collection efficiency is lower by about 10% than the baseline ash. This impaired ESP performance is likely due to high dust loading and fineness of the dust rather than due to high resistivities.

Soft deposit formation was observed on the furnace wall and heat exchanger surfaces which could be easily blown away by compressed air, suggesting that conventional soot blowing may suffice for full scale units.

Ash fusion temperatures of limestone injection waste was higher than that of base-line coal ash indicating that slagging is not expected to be a problem in full scale units. No slag formation was observed during the test program.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Under optimized operating conditions (Ca/S ratio = 3.0, particle mass median diameter = 8.6 μm and injection temperature ~1000° C) up to 43% of the sulphur dioxide can be removed from

flue gases while burning an eastern U.S. bituminous coal with sulphur content 1.7%, by injecting a Beachville limestone into the furnace cavity while simulating the Lakeview TGS quench rate of 536° C/S.

The process produces a finer and about 2.2 times as much waste as the base-line ash. The carbon content of the waste is high and 1.1% of the input heating value is estimated to be lost with the waste as compared to 0.7% for the base-line ash. Resistivity of the ashes produced are up to one order of magnitude higher than that of the base-line ash but remain well within the range where good precipitator performance is expected (resistivity $\sim 10^6$ ohm.cm). The ESP with a $15 m^2/m^3/S$ SCA performed with a 10% reduced efficiency, probably because of the fineness of the ash and increased dust loading.

Slagging does not appear to be a problem and the soft deposit formed on furnace walls and heat exchanger surfaces is easily removable suggesting that a more frequent use of conventional soot blowing equipment may be sufficient for full scale units. The limestone injection waste contains high levels of CaO, $CaSO_4$ and some $CaCO_3$, thus increased waste handling and disposal costs are expected.

It is recommended that the pilot scale development of the limestone injection process aimed at improving sulphur capture, sorbent utilization and ESP performance be continued.

Further work is recommended in the following areas:

1. Evaluation of the effect of residence time on sulphur capture by varying furnace quenching rate.

2. Evaluation of alternate sorbents such as high porosity limestone, dolomitic limestone, hydrated lime and sorbent additive mixtures.

3. ESP performance improvement by moisture and chemical conditioning.

4. Studying the effect of various injection modes, such as, inert gas, humid air blanket and sorbent water slurry injection.

5. Development work on the recycling and humidification of limestone injection waste to activate unreacted CaO for additional SO_2 removal, and better sorbent utilization.

6. Development work on limestone injection with fuel reburning, that is, injection of a secondary fuel above the main firing zone which produces free radicals which convert NO_x to N_2. Combining the two processes could result in a simultaneous SO_x to NO_x capture.

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APPENDIX I

RESPONSE SURFACES OF SULPHUR CAPTURE

by

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1. INTRODUCTION

In its effort to meet the commitment of reducing sulphur dioxide (SO_2) emissions, Ontario Hydro is currently considering various emission control methods. One of the concepts for SO_2 removal is the method of injecting calcium-based sorbents (such as limestones) into the furnace cavity of a coal-fired boiler. The idea is that SO_2 and calcium oxide (CaO) will react to form calcium sulphate which is solid and can be removed along with the ash. Since this process is in its early developmental stages, its effectiveness and feasibility needs to be demonstrated.

The Chemical Research Department has undertaken a pilot study to better understand the process of limestone injection. One of the main objectives of this study is to find conditions that will optimize the amount of sulphur (S) removed and the utilization of calcium (Ca). In the first phase of this study, a series of experiments were conducted to determine the percent of sulphur removed under various values of the following parameters:

- The temperature of the injection location;
- The size of the limestone particles;
- The calcium-sulphur mole ratio.

After the completion of the first phase of this study, the Statistics Unit was asked to determine a functional relationship between the percent of sulphur removed and the percent of calcium utilized and the above parameters. This function, called a response surface, may provide some understanding on the effect of the above variables on the process of sulphur removal and calcium utilization.

During the initial study of the data, it became apparent that it would not be possible to determine simultaneously the functional relationship of the three parameters with the percent of sulphur removed. Nevertheless, response surfaces of sulphur capture could be determined in two specific cases: (1) when the Ca/S mole ratio was fixed; and (2) when the injection location was fixed. This report documents the methodology used in and the results of the data analysis.

2. THE DATA

Because of the considerable cost for each experiment, only 3 to 5 different values for each of the variables were permitted. They were:

Injection location:

1. Location I3 - temperature = 850^{o}C
2. Location I2 - temperature = 1000^{o}C
3. Location I1 - temperature = 1200^{o}C
4. Location I0 - temperature = 1350^{o}C

Limestone particle size:

1. 4.4 micron
2. 8.6 micron
3. 10.5 micron

Calcium-sulphur mole ratio:

1. 1.5
2. 2.0
3. 2.5
4. 3.0
5. 4.0

Had an experiment been carried out for each of the combination of these values, there would have been 60 experiments. But this was not possible due to budgetary constraints. Only 25 experiments were performed. Table 1 summarizes the sulphur removal data collected from the experiment in the first phase.

Note that the percentages of calcium utilized are not given in the table. However, they can be easily derived from the following formula:

[Ca utilization (%)] = [S removal (%)] / [Ca/S mole ratio],

For example, for Injection location = I3, limestone particle size = 8.6 micron and Ca/S mole ratio = 3.0, the percentage of sulphur removed is 37%. Then the utilization percentage is 37%/3.0 = 12.33% .

3. THE METHOD

Let p denote the percent of sulphur removed, r the Ca/S mole ratio, s the size of the limestone particles, T the temperature of the injection location, u the utilization of calcium. In this exercise, the objective is to find the

algebraic functions f and k such that

$$p = f(s,r,T)$$

and

$$u = k(s,r,T).$$

To find these relationships one needs:

(a) to know the algebraic forms of the functions f and k;
(b) a set of data points (p_i,s_i,r_i,T_i), i = 1,2,..,n, such that there should be at least one observation of p at every pair of values of r (1.5 to 4), s (4.4 to 10.5) and T (850 - 1350).

As for condition (a), it is unlikely that the algebraic forms of f and k are known. However, they can be approximated by truncated Taylor series. For example, the function f can be approximated by

$$f^*(s,r,T) = a_0 + a_1 s + a_2 r + a_3 T + a_{11} s^2 + a_{12} sr + a_{13} sT + a_{22} r^2 + a_{23} rT + a_{33} T^2 \qquad (A)$$

The difference between f and f^* can be considered as noise and is assumed to be normally distributed with zero expectation and its variance is independent of s,r and T.

Now, the task is to estimate the coefficients in (A). To do so, the least-square criterion is used. The gist of this method is to find a set of coefficients $a_0,..,a_{33}$ which will minimize the sum of squares

$$L = \sum_i (p_i - f^*(s_i,r_i,T_i))^2 \qquad (B)$$

where $\{(p_i,s_i,r_i,T_i),\ i=1,2,..n\}$ is a set of observations that satisfies condition (b).

Condition (b) requires that, given any two parameters and their values, there should be at least one observation of sulphur removal percentage. For example, there should be at least one experiment performed at Ca/S mole ratio of 2 and injection location of I1. Now, it is clear from Table 1 that condition (b) was not satisfied. In other words, the above objectives can not be achieved.

Since this phase of the study has already been completed and no additional experiments would be performed, the objective of this exercise were slightly altered. The following two objectives, which are closely related to the original ones, can be achieved with the present set of data:

1. To find the function

$$p = g(s,T) \qquad (C)$$

for r = 3.

2. To find the functions

$$p = h(s,r) \qquad (D)$$

and

$$u = k(s,r) \qquad (E)$$

for T = 1000.

As before, it was assumed that g, h and k could be approximated by truncated Taylor series of two variables. For example, the function g(s,T) can be approximated by the polynomial

$$g^*(s,T) = a_0 + a_1T + a_2s + a_{11}T^2 + a_{12}Ts + a_{22}s^2 \qquad (F)$$

and the task is to find a set of coefficients that minimizes the sum of squared errors

$$L = \sum_i (p_i - g^*(s_i,T_i))^2$$

These polynomials are called response surfaces and a technique called response surface analysis is applicable to this problem. Such analyses can be performed by the RSREG procedure of the Statistical Analysis Systems (SAS) software package.

4. THE RESULTS

To find the response surface $g^*(s,T)$ which approximates the function g in (C) was a straightforward application of the RSREG procedure of SAS. The function $g^*(s,T)$ is given by (F), where

$$\begin{aligned} a_0 &= -199.318950000; \\ a_1 &= \quad 0.408229600; \\ a_2 &= \quad 9.667072220; \\ a_{11} &= -0.000203493; \\ a_{12} &= \quad 0.002133329; \\ a_{22} &= -0.915858856. \end{aligned}$$

The statistics of the analysis are given in Table 2. A response surface contour plot is given in Figure 3-12. In Table 2, the value R-square, which is the squared multiple coefficient of correlation, can be considered as a measure of fit for the function g^*. If it has a perfect fit, its R-square will be 100%. The worst R-square value is 0%. In this case, the R-square is 82%.

Table 2 also provides some other interesting observations. For example, the temperature factor has a significance level of 0.0159 while the size factor has a significance level of 0.1063. This means that the injection location temperature has more influence on the sulphur removal percentage than the particle size.

For the second response surface, it was apparent that the response of p to s and r could not be approximated by a second order polynomial. An appropriate transformation of the data was needed. Since the response of p to r has an initial rapid growth and then levels off, an exponential transformation of r seemed to be reasonable. Then, the function h in (D) becomes

$$p = h(s, e^{cr}) \qquad (G)$$

where c is some constant.

If c is known, then the RSREG procedure of SAS can be used to find the response surface of p as a function of s and e^{cr}. Otherwise, no procedure in SAS or other statistical packages is applicable. Therefore, a series of analyses, using the RSREG procedure with different values of c (ranging from -3.0 to 3.0), were performed to select the constant c that fits the data. It was concluded that, when $c = -1.5$ the response surface gave the best fit.

Table 3 provides the summary of the statistics in this analysis. The estimated function h^*, which has a R-square of 89%, is given by

$$h^*(s,r) = a_0 + a_1 s + a_2 e^{-1.5r} + a_{11} s^2 + a_{12} s e^{-1.5r} + a_{22} e^{-3r}$$

where
a_0 = 22.58384127;
a_1 = 7.94984636;
a_2 = -632.87947000;
a_{11} = -0.63621835;
a_{12} = 30.98037768;
a_{22} = 752.02840000.

A contour plot of this response surface is given in Figure 3-14. The data in Table 3 indicate that r is a more important factor than s.

For the response surface of calcium utilization (u), a straightforward RSREG procedure was carried out. The function, which has an R-square of 48%, is given by

$$k^*(s,r) = a_0 + a_1 s + a_2 r + a_{11} s^2 + a_{12} sr + a_{22} r^2$$

where $a_0 = -9.65666125;$
$a_1 = 1.78497801;$
$a_2 = 13.12439208;$
$a_{11} = -0.14776311;$
$a_{12} = 0.07419573;$
$a_{22} = -2.47953142.$

Table 4 provides the statistics of the analysis and Figure 3-16 is the contour plot of the response surface of k^*.

Clearly, an R-square of 48% is not a very good fit. This is not a surprise because the function h requires the transformation of r to $e^{-1.5r}$ and u is defined by u = p/r.

5. SUMMARY

Because condition (b) in Section 3 was not satisfied, the objective of finding the sulphur capture response surface f^* in (A) of the three variables (injection location, limestone particle size and Ca/S mole ratio) had to be slightly modified. Nevertheless, the alternatives, namely g^*, h^* and k^*, obtained from this exercise did provide some useful and interesting observations.

TABLE 1

RESULTS FROM PHASE I EXPERIMENTS
PERCENT OF SULPHUR REMOVED AFTER LIMESTONE INJECTION

Injection locations	Particle size (micron)	Ca/S mole ratio				
		1.5	2.0	2.5	3.0	4.0
I3 (850 C)	4.4					
	8.6				37	
	10.5				12	
I2 (1000C)	4.4		27	34 40	39 40	
	8.6	8 14	29	31 43	40 40	44
	10.5	17	17	30	32	
I1 (1200C)	4.4				28	
	8.6				18	
	10.5				11	
I0 (1350C)	4.4				24	
	8.6				18	
	10.5				11	

TABLE 2

STATISTICS OF RESPONSE SURFACE ANALYSIS
EFFECT OF INJECTION TEMPERATURE & PARTICLE SIZE
ON PERCENT OF SULPHUR REMOVED
(CA/S MOLE RATIO = 3.0)

RESPONSE MEAN	29.23077
ROOT MSE	5.664229
R-SQUARE	0.8267507
COEF OF VARIATION	0.1937763

REGRESSION	DF	TYPE I SS	R-SQUARE	F-RATIO	PROB
LINEAR	2	546.66280	0.4217	8.52	0.0133
QUADRATIC	2	516.93476	0.3988	8.06	0.0153
CROSSPRODUCT	1	8.12571407	0.0063	0.25	0.6302
TOTAL REGRESS	5	1071.72327	0.8268	6.68	0.0135

RESIDUAL	DF	SS	MEAN SQUARE
TOTAL ERROR	7	224.58442	32.08348892

PARAMETER	DF	ESTIMATE	STD DEV	T-RATIO	PROB
INTERCEPT	1	-199.31895	109.46337	-1.82	0.1114
TEMP	1	0.40822960	0.17019664	2.40	0.0476
SIZE	1	9.66707222	7.98888203	1.21	0.2655
TEMP*TEMP	1	-0.000203493	0.000069032	-2.95	0.0215
SIZE*TEMP	1	0.002133329	0.004239044	0.50	0.6302
SIZE*SIZE	1	-0.91858856	0.41772039	-2.20	0.0638

FACTOR	DF	SS	MEAN SQUARE	F-RATIO	PROB
TEMP	3	680.1656	226.7219	7.07	0.0159
SIZE	3	286.1089	95.36964	2.97	0.1063

TABLE 3

STATISTICS OF RESPONSE SURFACE ANALYSIS
EFFECT OF INJECTION PARTICLE SIZE & CA/S MOLE RATIO
ON PERCENT OF SULPHUR REMOVED
(INJECTION LOCATION = I2)

RESPONSE MEAN	30.29412
ROOT MSE	4.325983
R-SQUARE	0.8889387
COEF OF VARIATION	0.1427994

REGRESSION	DF	TYPE I SS	R-SQUARE	F-RATIO	PROB
LINEAR	2	1520.32617	0.8202	40.62	0.0001
QUADRATIC	2	100.31908	0.0541	2.68	0.1127
CROSSPRODUCT	1	27.02879410	0.0146	1.44	0.2547
TOTAL REGRESS	5	1647.67404	0.8889	17.61	0.0001

RESIDUAL	DF	SS	MEAN SQUARE
TOTAL ERROR	11	205.85537	18.71412483

PARAMETER	DF	ESTIMATE	STD DEV	T-RATIO	PROB
INTERCEPT	1	22.58384127	14.29635182	1.58	0.1425
SIZE	1	7.94984636	4.29742305	1.85	0.0914
EXPRATIO	1	-632.87947	216.50610	-2.92	0.0139
SIZE*SIZE	1	-0.63621835	0.31348584	-2.03	0.0673
EXPRATIO*SIZE	1	30.98037768	25.77852915	1.20	0.2547
EXPRATIO*EXPRATIO	1	752.02840	1369.16240	0.55	0.5938

FACTOR	DF	SS	MEAN SQUARE	F-RATIO	PROB
SIZE	3	91.9285	30.64283	1.64	0.2373
EXPRATIO	3	1415.02	471.6732	25.20	0.0001

TABLE 4

STATISTICS OF RESPONSE SURFACE ANALYSIS
EFFECT OF INJECTION PARTICLE SIZE & CA/S MOLE RATIO
ON PERCENT OF CALCIUM UTILIZATION
(INJECTION LOCATION = I2)

RESPONSE MEAN	12.11765
ROOT MSE	2.214966
R-SQUARE	0.4799114
COEF OF VARIATION	0.1827885

REGRESSION	DF	TYPE I SS	R-SQUARE	F-RATIO	PROB
LINEAR	2	19.87544478	0.1915	2.03	0.1782
QUADRATIC	2	29.83193410	0.2875	3.04	0.0889
CROSSPRODUCT	1	0.09048960	0.0009	0.02	0.8944
TOTAL REGRESS	5	49.79786848	0.4799	2.03	0.1523

RESIDUAL	DF	SS	MEAN SQUARE
TOTAL ERROR	11	53.96683740	4.90607613

PARAMETER	DF	ESTIMATE	STD DEV	T-RATIO	PROB
INTERCEPT	1	-9.65666125	18.35169207	-0.53	0.6092
SIZE	1	1.78497801	2.69435674	0.62	0.5500
RATIO	1	13.12439208	7.63587990	1.72	0.1136
SIZE*SIZE	1	-0.14776311	0.15306453	-0.97	0.3551
RATIO*SIZE	1	0.07419573	0.54631955	0.14	0.8944
RATIO*RATIO	1	-2.47953142	1.04006201	-2.38	0.0362

FACTOR	DF	SS	MEAN SQUARE	F-RATIO	PROB
SIZE	3	7.475432	2.491811	0.51	0.6849
RATIO	3	36.45816	12.15272	2.48	0.1158

APPENDIX II

Sample Calculation: Material Balance On Limestone Injection Waste

Basis: 100 kg coal

Ash = 87.8 g/kg

Baseline Ash (Composition)

	g/kg	wt. kg
$CaSO_4$	- 39	0.34
CaO	- 34	0.30
*Other ash Components	- 767	6.73
Carbon	- 161	1.41
		8.78

*Except CaO, $CaSO_4$ and C

LI Waste, RUN (LV-06)

S = 17 g/kg

wt. of waste produced = 20.16 kg

Ca/S ratio = 3
SO_2 capture = 40%
CO_2 in ash = 13 g/kg
Carbon in ash = 95 g/kg } by analysis

$$CaSO_4 \text{ in ash} = \underbrace{\frac{1.7}{32} \times 136 \times 0.4}_{\text{(formed)}} + \underbrace{0.34}_{\text{(inherent)}} = 3.23 \text{ kg}$$

$$CaCO_3 \text{ in ash} = \frac{3.0}{100} \times 20.16 = 0.60 \text{ kg}$$

$$\text{CaO in ash} = \underbrace{\frac{1.7}{32} \times 56 \times 3}_{\text{(formed)}} - \underbrace{\frac{1.7}{32} \times 56 \times 0.4}_{\text{(reacted with } SO_2\text{)}} + \underbrace{0.3}_{\text{(inherent)}} - \underbrace{\frac{0.60}{100} \times 56}_{\text{(reacted with } CO_2\text{)}} =$$

$$= 8.92 - 1.19 + 0.3 - 0.33 = 7.70 \text{ kg.}$$

COMPOSITION OF LI-WASTES

COMPONENTS	Run LV-06, Ca/S = 3.0			Run LV-01, Ca/S = 2.5		
	kg/100 kg Coal	Calculated g/kg	Analysis	kg/100 kg Coal	Calculated g/kg	Analysis
CaO	7.70	382	337	5.44	281	278
$CaSO_4$	3.23	160	150	3.44	178	136
$CaCO_3$	0.60	30	30	1.75	90	90
Other ash comp.	6.73	333		6.73	333	
Carbon	1.91	95	95	1.99	103	103
	20.16			19.35		

$$\text{Carbon in ash (sorbent free basis)} = \frac{\text{wt. of carbon}}{\text{wt. of inherent } (CaO + CaSO_4) + \text{wt. of other ash components} + \text{wt. of carbon}}$$

$$= \frac{1.91}{0.64 + 6.73 + 1.91} \times 100$$

$$= 21\%$$

APPENDIX III

Heat Losses Due to Carbon in Ash

(a) Baseline Ash (LV-02)

Basis: 100 kg coal

Ash = 8.78 kg
Carbon in Ash = 16.1%
Therefore Unburned Carbon = 8.78 x 0.161 = 1.41 kg
Fly Ash: Bottom Ash Ratio - 1:1
Since there is no carbon in bottom ash, then
unburned carbon = 1.41 x 0.5 = 0.71 kg
C.V. Fuel = 32.3 MJ/kg
Therefore 100 kg fuel = 3230 MJ
C.V. Carbon = 33.7 MJ/kg
Therefore Losses due to Carbon = 33.7 x 0.71 = 23.9 MJ

$$= \frac{23.9}{3230} \times 100 = 0.74\%$$

(b) Limestone Injection Ash (LV-06)

Basis: 100 kg coal

Ash = 20.1 kg
Carbon in Ash = 10.8%
Therefore Unburned Carbon = 20.1 x 0.108 = 2.17 kg
Fly Ash: bottom ash ratio -1:1
Since no carbon in bottom ash, then
unburned carbon = 2.17 x 0.5 = 1.08 kg
C.V. fuel = 32.3 MJ/kg
Therefore 100 kg fuel = 3230 MJ
C.V. Carbon = 33.7 MJ/kg
Therefore Losses due to Carbon = 33.7 x 1.08 = 36.4 MJ

$$= \frac{36.4}{3230} \times 100 = 1.1\%$$